Polymer Letters Edition

July 1973 Volume 11 Number 7

JOURNAL OF POLYMER SCIENCE

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The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition*, monthly; *Polymer Physics Edition*, monthly; *Polymer Letters Edition*, monthly; *Polymer Symposia*, irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition*, *Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

POLYMER LETTERS EDITION VOL. 11, PP. 427–434 (1973)

THE HYDROGENATION OF A POLYPENTENAMER AND THERMAL PROPERTIES OF THE RESULTING PRODUCTS

Introduction

The hydrogenation of various polymers containing unsaturation has been investigated for many years (1). For example, using this technique it is possible to alter the properties of polybutadiene from those of an elastomer to those of a plastic bearing some resemblance to polyethylene. Early hydrogenation techniques usually involved heterogeneous catalysts or highly reactive chemicals, methods which were subject to considerable disadvantages from a technological point of view and which generally resulted in appreciable degradation to the polymer chain backbone. More recently, a noncatalytic technique has been developed which involves diimide hydrogenation and is carried out homogeneously (2,3). It appears that this procedure has the advantage of minimizing side reactions and that hydrogenation can be carried to completion without backbone degradation.

It is well known that polybutadiene prepared anionically always contains a certain quantity of vinyl side groups, the lowest attainable quantity being of the order of 8%. Hydrogenation of this material, therefore, leads to a product comparable to some low density polyethylenes or ethylene-butene copolymers rather than to a product comparable to linear polyethylene. It was the objective of the present study to prepare derivatives of linear unsaturated polymers of varying degrees of hydrogenation so as to progress from an amorphous material on the one hand to highly crystalline linear polyethylene on the other and to investigate in detail the property changes resulting from this procedure. It was, therefore, decided not to hydrogenate polybutadiene, but rather a polymer prepared by the ring-opening polymerization of cyclopentene. Such polymers are generally referred to as polypentenamers. This report outlines the hydrogenation procedure, the characterization of the products, and some thermal properties of the crystalline derivatives as determined by differential scanning calorimetry (DSC). Subsequently, the results of a detailed X-ray analysis and mechanical properties study will be published.

Experimental

Materials

a. Toluenesulfonyl hydrazide (TSH)

Commercial TSH was purified by recrystallization from ethanol, dried in vacuo at 30°C for 12 hours and stored under nitrogen in the dark.

b. Polypentenamer (PP)

This polymer was prepared and kindly provided by the Goodyear Tire and

TABLE I

Polymer	Elemental Analysis				Molecular Weight			
	C (%)	H (%)	0 (%)	S (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_z \times 10^{-3}$	$\frac{M_w}{M_n}$
PP found	87.74	11.92	0	0	94.4	172	267	1.83
Calculated for C_5H_8	88.24	11.76	0	0				
Hydrogenated PP found	85.79	14.31	0	0	105	184	289	1.75
Calculated for C_5H_{10}	85.72	14.28	0	0				

Rubber Company. On the basis of infrared analysis (4) it was determined that approximately 82% of the double bonds in the polymer were in the trans configuration, 17% were in the cis configuration, and < 1% vinyl side groups were present. The nominal molecular weight distribution was determined by gel permeation chromatography (GPC) using the polystyrene calibration and the results were: M_n = 94,400; M_w = 172,300; M_w/M_n = 1.83.

c. Solvents were Purified by Standard Procedures

2. Hydrogenation

PP (0.0185 M) was dissolved in 300 ml of p-xylene at 80°C under nitrogen. To this solution was added sufficient TSH to give a 2.0 mole ratio of TSH to PP repeat units. The resulting mixture was heated with stirring to 135°C under nitrogen. Nitrogen was evolved from the reaction mixture at 130°C and a yellow color was gradually developed. Aliquots of 30 ml were removed from the reaction mixture at specified times and the polymers were isolated by precipitation from methanol. After washing with methanol, water, and more methanol, the hydrogenated polymers were purified by reprecipitation from p-xylene solutions into methanol and then dried at room temperature in vacuo for 48 hours.

Polymer characterizations were carried out on the basis of elemental analysis, infrared analysis, and GPC. Table I summarizes the results for the starting PP and the completely hydrogenated product.

Property Measurements

Films suitable for infrared and DSC measurements were prepared by casting from p-xylene at 80°C.

Infrared analyses were carried out using a Perkin Elmer Model 180 infrared spectrophotometer. The determination of the double bond configurations present in the starting PP was carried out on the basis of the absorption bands at 10.35 μm (trans.), 11.0 μm (vinyl) and 7.12 μm (cis) using standard calibration procedures available in the literature (4). The disappearance of trans double bonds in the hydrogenated products was followed using the 10.35 μm absorbance. Weight-fraction crystallinity in the hydrogenated products was determined from the ratio of the 730 cm^{-1} peak absorbance to the 720 cm^{-1} peak absorbance according to the method of Stein and Sutherland (5).

DSC measurements were carried out on a Perkin-Elmer Instrument, Model DSC-1B. The scanning speed was 10°C per minute in all cases and pure benzoic acid was used as a standard. The temperature range was from room temperature to ca. 150°C. The temperature of maximum excursion of the melting endotherm from the base line was taken to be the melting point of the pure polymers. Heats of fusion were determined from areas under the melting endotherms.

Polymer-decalin mixtures were prepared by first adding a known volume of decalin with a calibrated microsyringe into a sample pan and weighing; 4 mg of polymer were then added and the pan was crimped shut. The melting temperature was then determined in the normal way.

Film densities were determined using a water-ethanol density gradient column at 23°C.

TABLE II

Properties of Hydrogenated PP

Hydrogenation Time (min)	Residual trans double bonds (%)	T_m (°C)	Density	Enthalpy of Fusion ΔH_f cal/g	Enthalpy of Fusion ΔH_u cal/g	Density	Percent Crystallinity IR	Percent Crystallinity DSC
0	100	–	0.879	–	–	–	–	–
10	84	–	0.914	–	–	–	–	–
20	49	81	0.917	17	35	57	57	49
30	18	111	0.940	36	49	69	76	73
40	9	122	0.942	34	46	70	80	74
60	1	128	0.957	42	52	77	81	81
120	0	129	0.967	46	54	82	82	85
180	0	130	0.971	51	59	84	85	86

Results and Discussion

It is clear from Table I that no degradation occurs as a result of hydrogenation and that no other side reactions take place. In Table II are collected some properties of partially hydrogenated and wholly hydrogenated samples of PP. These range from the completely amorphous starting material to a polymer of 85% crystallinity with a melting point of 130°C. It is to be noted that the diimide hydrogenation reaction proceeds somewhat more rapidly with cis double bonds than with trans double bonds and that no detectable cis double bonds remain after 20 minutes of reaction time. Therefore, the residual trans double-bond content listed in Table II represents essentially the entire amount of unsaturation present in the polymer, with the exception of the 10-minute sample, which has a small cis content.

The enthalpies of fusion reported in Table II are determined in the following manner: ΔH_f is obtained from the area under the DSC melting endotherms; and ΔH_u, by the so-called diluent method, that is, from the melting point depression observed in the presence of decalin. The relation between the melting point depression and ΔH_u was first given by Flory (6).

$$1/T_m - 1/T_m^{\circ} = (R/\Delta H_u)(V_u/V_1)(v - \chi_1 v_1{}^2)) \tag{1}$$

In eq. (1), T_m is the melting point in the presence of diluent, $T_m{}^{\circ}$ is the melting point of undiluted polymer, V_1 is the molar volume of solvent, V_u is the molar volume of the polymer repeat unit, and χ_1 is the polymer-solvent interaction parameter. In these polymers, V_u was taken to be 16.4 cm^3/mole of repeat units and V_1 was taken to be 159 cm^3/mole. $T_m{}^{\circ}$ was obtained from the extrapolated intercept of a plot of $1/t_m$ versus v_1. The weight percent crystallinities are derived from the densities by using a correlation for polyethylene developed by Sperati, Franta, and Starkweather (7). The same quantities are obtained from infrared measurements as described in the experimental section. The values reported under the column headed "DSC" were derived from the approximate relation

$$X = (\Delta H_f/\Delta H_u) \times 100 \tag{2}$$

where X is the weight-percent crystallinity.

The behavior of T_m and ΔH_u as a function of hydrogenation noted in Table II is typical of that of ethylene copolymers containing a wide variety of substituents. These include chlorine (8), alkyl side branches (9), acetate side groups (9a) and many others (10). The depression of the melting point due to the presence of noncrystallizable substituents has been treated theoretically, leading to the well-known expression (11)

$$1/T_m - 1/T_m^{\circ} = -(R/\Delta H_u) \ln (1 - x_B) \tag{3}$$

where x_B is the mole fraction of comonomer units present, T_m is the melting point of the copolymer, and $T_m{}^\circ$ is the melting point of the pure homopolymer. It is to be noted that eq. (3) cannot be quantitatively applied to the experimental data presented here owing to the fact that eq. (3) refers to equilibrium conditions which are certainly not realized. However, it has been shown recently by Sanchez and Eby (12) that it is impossible to distinguish between the model represented by eq. (3), and one in which the comonomer units are included in the crystal lattice on the basis of melting point data alone.

Turning to the data on enthalpy of fusion, Sanchez and Eby (12) are able to distinguish two limiting cases. On the one hand we have the situation where the comonomer units are present in the lattice, and this leads to the following expression for the enthalpy of fusion of a lamellar crystal

$$\Delta H_f/X = \Delta H - x_B \Delta H_d - 2\Delta H_e/\ell \tag{4}$$

In eq. (4), X is the weight fraction crystallinity, ΔH is the enthalpy of fusion of the perfect crystal, ΔH_d is the excess enthalpy associated with the formation of a defect in the crystal lattice. ΔH_e is the excess enthalpy associated with forming the basal surfaces of the lamellar crystal, and ℓ is the lamellar thickness of the crystal.

On the other hand, in the case where the comonomer units are completely excluded from the crystal lattice, we have

$$\Delta H_f/X = \Delta H - 2\Delta H_e/\ell \tag{5}$$

It follows that for the model represented by eq. (4) (inclusion model)

$$\Delta H_u = \Delta H - x_B \Delta H_d \tag{6}$$

and for the model represented by eq. (5) (exclusion model)

$$\Delta H_u = \Delta H \tag{7}$$

It is perhaps worth noting that the measured ΔH_u values are appropriate for a crystal of infinite thickness. This has been discussed previously (8).

It is immediately apparent that the exclusion model cannot be correct either for the hydrogenated materials or the other copolymers of polyethylene for which ΔH_u has been determined, since they all show a strong dependence of ΔH_u on the concentration of comonomer units. However, the linear dependence on x_B required by eq. (6) is not observed, implying that the correct model for these copolymers lies somewhere between the two extremes. There is good evidence that in the case of the chlorine-containing polymers (8) and also in a series of ethylene-phosphonic acid copolymers (13), the substituents are heavily concentrated at the fold surfaces. It is reasonable to assume that this is also the case with the double bonds in the partially hydrogenated PP. Con-

firmation of this must await further X-ray and electron microscope studies presently underway.

From the above discussion, it is apparent that the exact form of eq. (2) is

$$X = \{\Delta H_f/(\Delta H_u - 2\Delta H_e/\ell)\} \times 100 \qquad (8)$$

Since data on ℓ are lacking, it is impossible to estimate the magnitude of the term $2\Delta H_e/\ell$, and thus the error involved in the use of eq. (2) to determine X is unknown. The relatively good agreement among the crystallinity values quoted in Table II indicates that $2\Delta H_e/\ell$ is small for this series of polymers.

The authors are grateful to the National Science Foundation (Grant 33129X) and the U.S. Army (contract DAA6-46-47-C-0076) for supporting this research. We are also grateful to Dr. K. W. Scott for supplying the PP sample and to Professor I. Sanchez for helpful discussions.

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Received February 26, 1973

THE EFFECT OF SOLVENT CONCENTRATION ON THE CRYSTALLIZATION OF POLYETHYLENE UNDER ELEVATED PRESSURE

The crystallization of polyethylene under hydrostatic pressures above about 3000 bar has been studied extensively in our laboratory (1–5). One of the major results was that on crystallization from dilute solution, little effect of pressure on the fold length of the lamellae formed could be detected (1), while crystallization under identical conditions from the melt led to extended-chain crystals (2–5). Copolymerizing the ethylene with propylene or 1-butene affected the crystallization to extended-chain crystals from the melt so that samples with only about two or more side-groups per 100 CH_2-chain units developed no extended-chain crystals (2). During the last year we investigated in

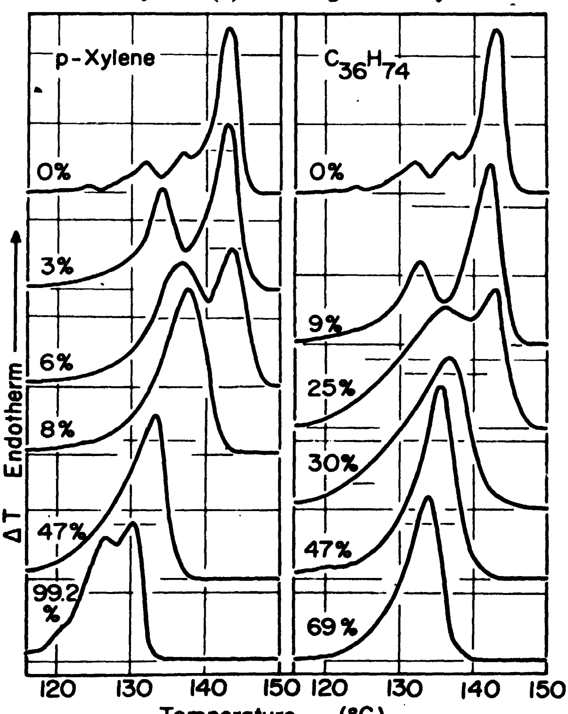

Fig. 1. DTA traces of polyethylene crystallized at 4150 bar in the presence of the indicated weight percentages of solvent (cooling rate ca. 4°C/hr). Analysis was carried out at heating rates of 10°C/min after removal of the solvent under conditions having minimal effect on the crystal morphology. The curves represent only approximately equal weights of sample.

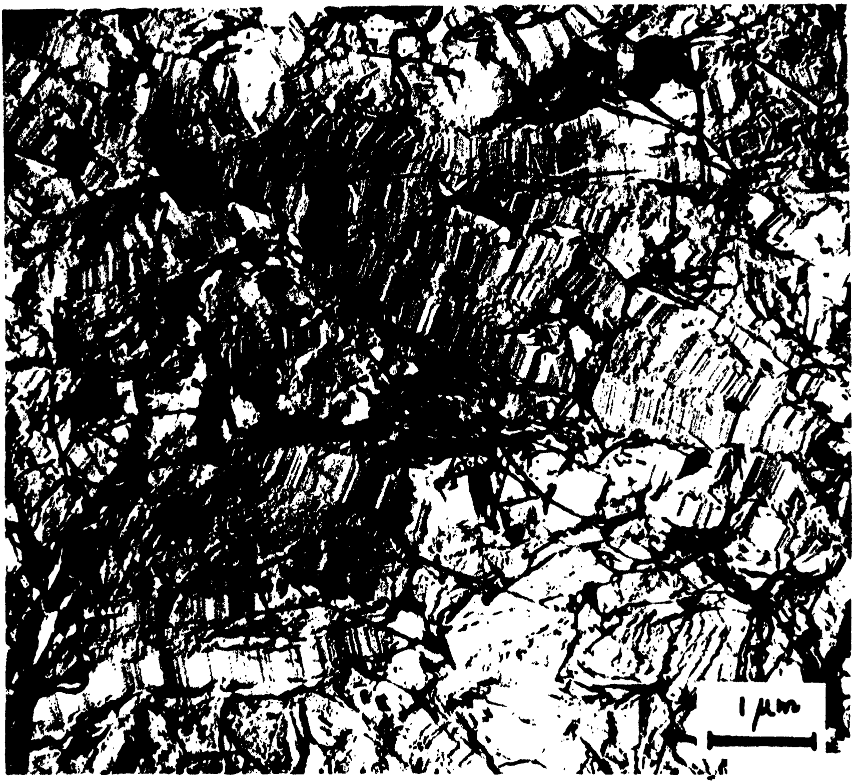

Fig. 2. Electron micrograph of a fracture surface of polyethylene pressure-crystallized in the presence of 6% p-xylene by weight.

more detail the effect of increasing amounts of solvent on crystallization at elevated pressure. In this letter we would like to report the effect of different concentrations of p-xylene and hexatriacontane on the crystallization of polyethylene at elevated pressure. A surprisingly small amount of solvent will be shown to inhibit chain extension.

Mixtures of polyethylene and p-xylene were prepared by enclosing the appropriate weights of material in brass bellows. The linear polyethylene was the standard material M used in prior investigation with a weight average molecular weight of 153,000 and a polydispersity of 18. The mixture was heated with repeated turning to 130°C under its own vapor pressure for 24 hr to achieve dissolution. Crystallization was carried out subsequently under 4150 bar pressure by slow cooling (ca. 4°C/hr) from 220°C. Samples 100, 97, 94, 92, 90, 78, 66, 53, 10, 0.8, and 0.11% polyethylene by weight were prepared.

Polyethylene-hexatriacontane mixtures were preheated to 170°C under their own vapor pressure for 3 days. Crystallization was done as in the case of the mixtures with p-xylene. Samples of 100, 91, 87, 75, 70, 53, 44, 31, and 10% polyethylene by weight were prepared.

Fig. 3. Electron micrograph of a fracture surface of polyethylene pressure-crystallized in the presence of 8% p-xylene by weight.

The pressure, applied at 220°C, was close to hydrostatic by using the pressurestat described previously (4). After completion of crystallization the solvents were removed. The hexatriacontane was dissolved at 60°C in p-xylene and residual p-xylene was evaporated under high vacuum. The analysis involved interference microscopy for the dilute solution samples (2), DTA of most samples (2,4), and electron microscopy of two-stage replicas of the samples with high polyethylene content (5). Details of these techniques are given in the references quoted. Thermal analysis was carried out on a duPont Model-990 differential thermal analyzer with DSC attachment.

Figure 1 displays typical results obtained by DTA at a heating rate of 10°C/min. The pressure-crystallized pure polyethylene separates into extended-chain mixed crystals of molecular weight 10,000 and higher showing a melting peak temperature of 142-143°C (4). This high peak temperature results from superheating of the extended-chain mixed crystals (6). The dilatometric melting point of such extended-chain crystals of the polymer used here was shown to be 138.3°C (2,4). The small peaks at somewhat lower temperature represent segregated fully extended chain crystals of molecular weights below 10,000 (4).

Fig. 4. Electron micrograph of a fracture surface of polyethylene pressure-crystallized in the presence of 31% hexatriacontane ($C_{36}H_{74}$) by weight.

On the addition of only a little p-xylene, the sample changes. An increased amount of lower-melting polymer is produced and the extended-chain portion is reduced. About 8% of the solvent is sufficient to cause the peaks due to extended-chain crystals to disappear from the DSC traces in Figure 1. These DSC results are confirmed by electron microscopy of replicas of fracture surfaces. Figures 2 and 3 indicate the rapid decrease of extended-chain crystals on increasing the p-xylene concentration from 6 to 8%. The easily recognizable striated extended-chain lamellae (3,5) are of increasingly smaller thickness and perfection on increasing solvent content, and disappear completely above 8% concentration of solvent. Between the lamellae, less well defined crystal morphology was found, usually representative of lamellae of smaller fold length which on fracture draw and obliterate any clear structure. The lower DTA melting peak shows a temperature of 137-138°C, typical of well crystallized polyethylene (6). Increasing amounts of solvent lower this melting peak temperature further to about 133°C for 47% p-xylene. This temperature is identi-

cal with that of melt-crystallized polyethylene at atmospheric pressure, in which the fold length is about 250 Å (7). At even higher solvent concentration, typical behavior of solution-grown polyethylene lamellae is obvious. A double-peaked melting curve as shown in Figure 1 is characteristic of large-scale rearrangement before and during melting. The two peak temperatures at about 126 and 130°C are in line with data obtained from well crystallized lamellae from more dilute solution (7). Interference microscopy revealed lamellar crystals, as reported earlier for dilute solution crystallization under elevated pressure (1).

The data on the polyethylene-hexatriacontane mixtures are similar, but extended-chain crystals can be detected to about 3-4 times the weight percentage concentration of the p-xylene solvent. Also, there is a slower decrease in melting peak temperature with increasing concentration. Figure 4 illustrates that at 31% hexatriacontane by weight occasional extended-chain lamellae are still present. On a molar basis the effects of the two solvents are more closely similar.

To summarize, only a little p-xylene is necessary to prevent extended-chain crystallization of polyethylene under high pressure. Increasing amounts of solvent lower the melting peak temperature as crystals of intermediate perfection are formed; and finally the familiar low-melting, metastable lamellae, approximately 150 Å thick, which undergo extensive rearrangement on heating, are produced. Although hexatriacontane is chemically similar to polyethylene, it can be tolerated to a larger weight percent concentration.

In the framework of our explanation of crystallization of polyethylene to extended-chain crystals under pressure, we speculate that small amounts of solvent permit improved initial crystallization (molecular nucleation) which restricts the subsequent chain extension in the solid state (4). The effect of low molecular weight solvents on crystallization of polyethylene under elevated pressure should be different from the restriction of chain extension found by copolymerization with branched repeat units. In the latter case it is probable that chain extension is hindered by interference of the branches with the chain extension mechanism.

This work was supported through a NATO fellowship to one of the authors (G.T) and by a grant of the General Electric Company. This financial help is gratefully acknowledged.

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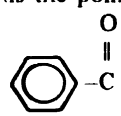
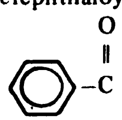
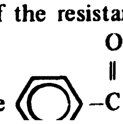
Received April 25, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 441–447 (1973)

EFFECT OF THE TEREPHTHALOYL RESIDUE ON CHAIN FLEXIBILITY OF POLY(ETHYLENE TEREPHTHALATE)

Williams and Flory (1) have shown that the two coplanar arrangements (trans and cis) of the carbonyl groups and the benzene ring in the terephthaloyl residue are equally likely and are the most probable conformers. Consequently, they concluded that the virtual bond spanning the benzene ring and connecting the carbonyl carbons behaves as a statistical freely rotating link (2) between the ethylene glycol segments of the poly(ethylene terephthalate) (PET) chain.* This model of the terephthaloyl residue yielded calculated chain dimensions in agreement with the values obtained from dilute solution intrinsic viscosity studies (3,4).

Since the mechanical and dielectric properties of polymers depend on the rates of transition between various chain conformations, it is of interest also to examine the barriers hindering the motion of the terephthaloyl residue in PET, which affect its dynamic properties. Inspection of space-filling molecular models confirms the point argued by williams and Flory (1), that the rotations about the  bonds adjoining a benzene ring (see Fig. 1) are independent of each other (due to separation by a benzene ring) and of the rotations about the $O{-}CH_2$ and $CH_2{-}CH_2$ bonds (due to separation by a planar trans ester bond). Consequently, the net rotation angle ϕ about the virtual bond (see Fig. 1) spanning the terephthaloyl residue is a sum of the two independent rotations ϕ_1 and ϕ_2 about  bonds terminating this virtual bond.

Estimation of the resistance to rotation $V_{\phi_{1,2}}$ (the subscript meaning ϕ_1 or ϕ_2) about the  bonds in the terephthaloyl residue is accomplished

*The distinction between a statistical freely rotating link or bond and a true or dynamical freely rotating link is easily illustrated. Any bond about which exist a small number of symmetrically located rotational minima of equal energy will behave as a statistical freely rotating link. However, since there are barriers between the rotational minima, the link is not true or dynamical freely rotating, because all rotational states about the link are not accessible and equally probable.

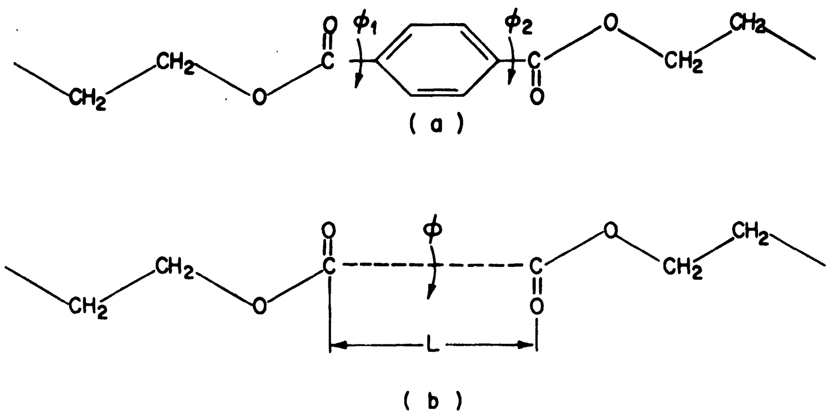


Fig. 1(a). Schematic representation of a portion of the PET chain encompassing a terephthaloyl residue. The planar zigzag conformation with a trans arrangement of carbonyl groups is taken as the reference state, where $\phi_1 = \phi_2 = 0$ in this state, and the angles are positive for right-handed rotations (2). (b) PET chain as in (a) except the benzene ring in the terephthaloyl residue is replaced by the virtual bond L: ϕ is 0 in this reference trans state and positive for right-handed rotations (2).

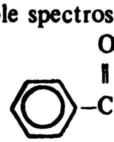
by considering two independent contributions: 1) the nonbonded interactions V_{nb} of the ester group with the carbon and hydrogen atoms ortho to the ester group and 2) the intrinsic twofold torsional potential V_π resulting from the delocalization of π-electrons to span both ester groups and the intervening benzene ring.

$$V_{\phi_{1,2}} = V_{nb} + V_\pi \tag{1}$$

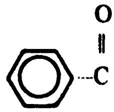
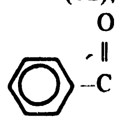
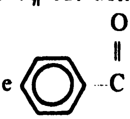
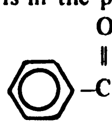
$$V_{nb} = \sum_{i,j} \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \tag{2}$$

$$V_\pi = (V_\pi^\circ/2)(1 - \cos 2\phi_{1,2}) \tag{3}$$

A 6-12 potential (5,6) is used to evaluate the nonbonded interactions V_{nb}, while the magnitude of the barrier V_π° in the intrinsic π-electron resistance to rotation is estimated as follows.

There appear to be no available spectroscopic data bearing directly upon the barrier to rotation about the  bonds in the alkyl terephthalate esters. However, the barriers about the same bond have been determined (7-10) in the case of benzaldehyde and several of its para-substituted derivatives.

In the liquid phase the barrier obtained from far-infrared spectroscopy (7-9) is 6.4-6.7 kcal/mole for benzaldehyde. The presence of the electron-donating (11) groups CH_3--O and $(CH_3)_2$–N groups in the para position increase (10) this barrier by about 1.3 and 2.9 kcal/mole, respectively.

If the barrier about the  bond in benzaldehyde is also separated into the contributions made by the nonbonded interactions V_{nb} and the π-electron delocalization V_π, then it is found (see eqs. (1)-(3)) that V_{nb} is 0.7 and 0.0 kcal/mole for $\phi_{1,2}$ = 0 or 180° and 90 or 270°, and by difference $V_\pi = V_\pi^\circ = V_{\phi_{1,2}} - V_{nb}$ is 7.1 to 7.4 kcal/mole at $\phi_{1,2}$ = 90 or 270°. (The geometries of benzaldehyde and terephthalate ester used in the calculations of V_{nb} are taken from ref. (8) and Bowen and Sutton (12), respectively.) The same contribution V_π° to the barrier about the  bond in the terephthaloyl residue should be several (2.0 or 3.0) kcal/mole smaller than V_π° for benzaldehyde, because of the reduction in the π-electron density of the  bond in terephthalates due to the partial double bond character of the ester bond $(\overset{O}{\overset{\|}{C}}-O)$, and because in the terephthaloyl residue another ester group, which is an electron withdrawing group (11), is in the para position thereby further reducing the π-electron density of the  bond.

Hence, we feel a reasonable estimate of the π-electron delocalization barrier in the terephthaloyl residue to be $\leq$ 5.0 kcal/mole. However, it must be stressed that none of the conclusions drawn concerning the flexibility of the terephthaloyl residue are qualitatively affected if V_π° should be as large (7-7.5 kcal/mole), as it appears to be in benzaldehyde. We are presently attempting to measure this barrier in terephthalate esters and in para-substituted benzoates by nuclear magnetic resonance spectroscopy.

Figure 2 presents a plot of $V_{\phi_{1,2}}$ as a function of ϕ_1 or ϕ_2, where V_π° = 5.0 kcal/mole. The twofold character of $V_{\phi_{1,2}}$ is apparent, with barrier heights of about 3.0 kcal/mole. (For purposes of comparison the dashed line in Fig. 2 is obtained from eq. (3) with V_π° = 2.95 kcal/mole by neglecting the nonbonded interactions.) It is the nonbonded interactions which favor out-of-plane benzene and ester group conformations (V_{nb} = 0.0 for $\phi_{1,2}$ = 90, 270°

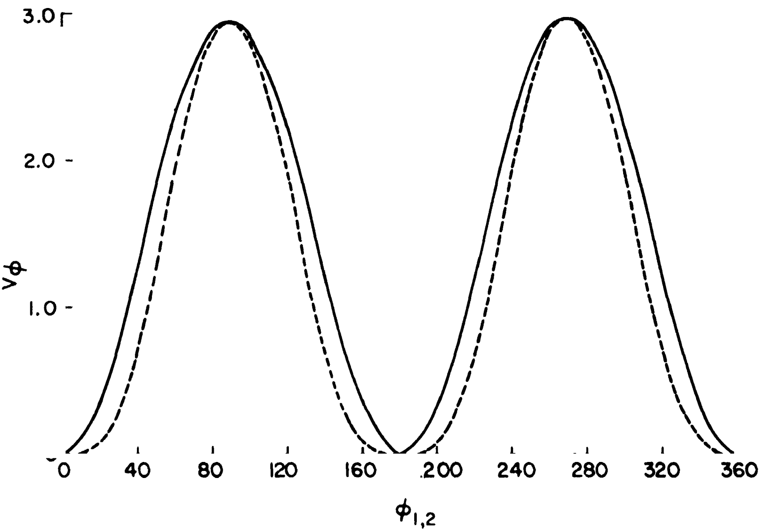
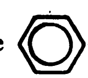


Fig. 2. Potential energy $V_{\phi_{1,2}}$ (kcal/mole) for rotation $\phi_{1,2}$ about the $\rangle\!-\!\overset{O}{\overset{\|}{C}}$ bonds in the terephthaloyl residue. The solid line corresponds to

$V_{\phi_{1,2}} = V_{nb} + V_\pi$, where $V_\pi^\circ = 5.0$ kcal/mole, and the dash lined is given by $V_{\phi_{1,2}} = V_\pi$, where $V_\pi^\circ = 2.95$ kcal/mole.

and 2.0 kcal/mole for $\phi_{1,2} = 0, 180^\circ$) and which partially cancel the π-electron delocalization barrier ($V_\pi = 0.0$ for $\phi_{1,2} = 0, 180^\circ$ and 5.0 kcal/mole for $\phi_{1,2} = 90, 270^\circ$).

The net rotation ϕ about a terephthaloyl residue virtual bond is a sum of two independent rotations $\phi_1 + \phi_2$ about the  $-\overset{O}{\overset{\|}{C}}$ bonds. As a result, the probability f_ϕ of a virtual bond rotational state ϕ is simply the product of the independent probabilities of rotational states ϕ_1 and ϕ_2.

$$f_\phi = (SW_{\phi_1})(SW_{\phi_2}) / \sum_{\phi_1,\phi_2} (SW_{\phi_1})(SW_{\phi_2}) \tag{4}$$

$$SW_{\phi_1 \text{ or } 2} = \sum_{\phi_1 \text{ or } 2} \exp(-V_{\phi_1 \text{ or } 2}/RT) \tag{5}$$

In Table I the fractional probabilities f_ϕ of the virtual bond rotational states ϕ calculated when $V_\pi^\circ = 5.0$ kcal/mole and $T = 25°C$ are presented. It is apparent that every virtual-bond rotational state is appreciably populated. In fact, the maximum energy difference between any two rotational states about the virtual bond L is 1.65 kcal/mole at 25°C (a true freely rotating link possesses no rotational barriers).

TABLE I

Probabilities of Rotational States about the Virtual Bond Spanning a Terephthaloyl Residue in PET

ϕ (deg)	f_ϕ
0,180	0.0574
10,170,190,350	0.0550
20,160,200,340	0.0487
30,150,210,330	0.0399
40,140,220,320	0.0302
50,130,230,310	0.0209
60,120,240,300	0.0130
70,110,250,290	0.0076
80,100,260,280	0.0044
90,270	0.0035

It is clear from the symmetry of the distribution of virtual-bond rotational states that the terephthaloyl residue should behave as a statistical freely rotating link (2) in PET as noted by Williams and Flory (1). However, instead of being confined predominantly to the planar conformations $\phi = 0°$ (trans) and 180° (cis), rotations about the terephthaloyl residue virtual bond resulting in nonplanar conformations are also highly probable. Thus, it appears that the terephthaloyl residue in PET closely approximates a true freely rotating link in the dynamic as well as the statistical sense, because of the low barriers separating the rotational states, all of which are appreciably accessible.

A laser-Ràman study of PET recently reported by Melveger (13) supports the proposal of nonplanar terephthaloyl residue conformations presented here. On the basis of the observed broadening of the C=O stretching band with a decrease in crystallinity, Melveger suggested that the carbonyl groups may be rotated out of the plane of the benzene ring in amorphous PET.

The ability of the terephthaloyl residue to adopt low-energy nonplanar conformations leads to several important consequences for the PET chain. From among the equilibrium properties of PET only those dependent upon the polarizability of the terephthaloyl residue should be sensitive to its possible nonplanar nature. Hence, the optical properties of PET should reflect the possibility of assuming nonplanar terephthaloyl conformations, while equilibrium proper-

erties such as the dimensions and the mean-square dipole moment* of PET should be unaffected.

Possibly the most important consequence of a flexible terephthaloyl residue is its effect on the dynamic properties of PET. Easily accessible, nonplanar terephthaloyl residue conformations separated by relatively low intramolecular barriers (see above) would be expected to result in dynamic characteristics for PET quite in contrast to those anticipated for a rigid, planar terephthaloyl residue. In light of this finding, it is suggested that the dynamic-mechanical and dielectric properties of PET should be reinterpreted.

The author is grateful to Drs. E. A. Chandross, G. N. Taylor, and A. M. Trozzolo for several helpful discussions, and to Dr. E. P. Otocka for bringing to my attention ref. (13).

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*The dipole moments of dimethyl and diethyl terephthalate calculated from the measured moments (14) of methyl and ethyl benzoate (see ref. (1)) by averaging over ϕ rotations according to the f_ϕ of Table I are 2.39 and 2.45D, respectively, which compare favorably with both the experimental values (15) of 2.30 and 2.42D and those calculated by Williams and Flory (1), 2.34 and 2.41D, assuming equally probable planar conformations for these terephthalate esters.

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Received April 16, 1973
Revised June 18, 1973

POLYMER LETTERS EDITION

VOL. 11, PP. 449–452 (1973)

300 MHz PROTON NMR OF POLYBUTADIENE: MEASUREMENT OF cis-trans ISOMERIC CONTENT

High resolution ^{1}H NMR has previously been used to determine cis-trans ratios in a few polymers (1,2), but it has not been suitable for determination in the case of polybutadiene (3). With the advent of NMR spectrometers capable of operating at 300 MHz and attaining resolution of 1 Hz or less, it becomes possible to determine the 1,4-cis, 1,4-trans, and 1,2 contents of polybutadienes.

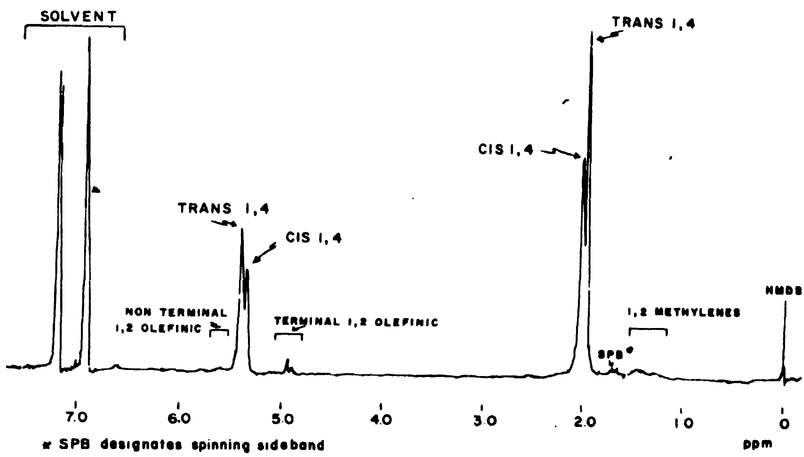

Fig. 1. ^{1}H NMR spectrum at 300 MHz of an n-butyllithium catalyzed polybutadiene in o-dichlorobenzene solution at 100°C. Hexamethyldisiloxane is the reference.

Figure 1 depicts the 300 MHz ^{1}H NMR spectrum of an organlithium-polymerized polybutadiene, of approximately 9 mole % 1,2 content, in orthodichlorobenzene solution. The spectrum was recorded at +110°C and hexamethyldisiloxane was used as the internal standard. The general features of the spectrum have been previously defined (4), i.e., the resonance groupings centered at 1.3, 2.0, 4.8, 5.4, and 5.6 ppm represent 1,2 methylene, 1,4 methylene, 1,2 terminal vinyl, 1,4 olefinic, and nonterminal vinyl protons, respectively. However the 300 MHz spectrum contains features in both the aliphatic and olefinic proton regions that are not apparent in spectra recorded with lower field spectrometers. In particular, the backbone methylene proton resonance of the 1,4 units (2.0 ppm) is observed as two peaks at this sweep width. A comparison of the chemical shifts shown in Table I of a high cis (ca. 98%) and

TABLE I

Chemical Shifts of Resonance Peaks Representing cis-trans Isomer in Poly(butadiene)

Polymer	Chemical Shift, ppm[a] Aliphatic trans	Aliphatic cis	Olefinic cis	Olefinic trans
Highly cis (98%)	1.97	2.03	5.33	not detected
Highly trans (>90%)	1.99			5.36
LM-207 Butyl lithium catalyzed	1.98	2.03	5.32	5.37

[a]With reference to hexamethyldisiloxane at +110°C in o-dichlorobenzene solvent containing 10-15% W/V polymer.

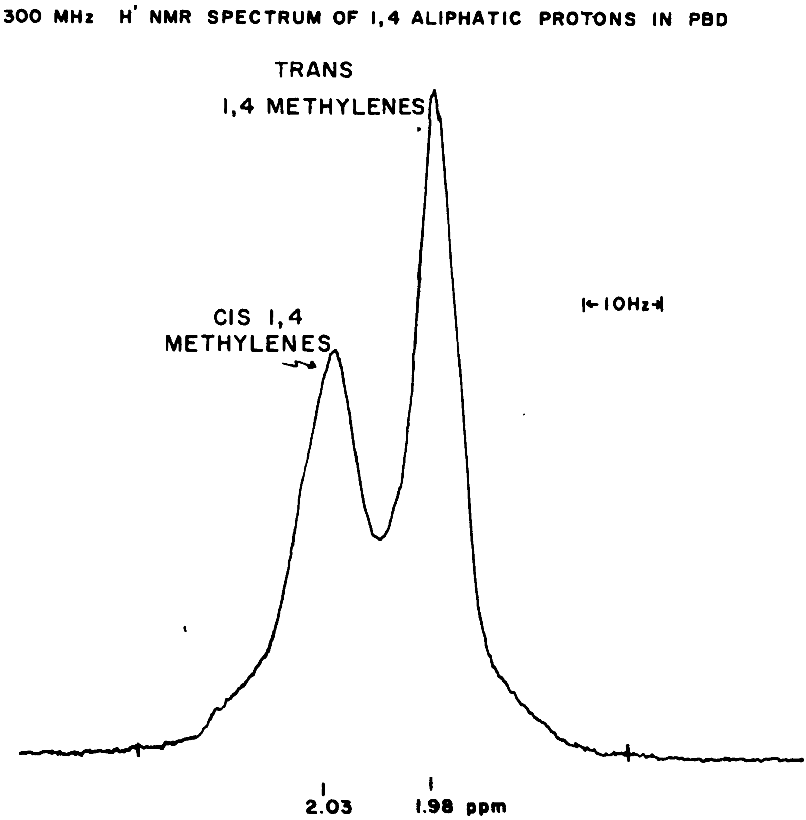

Fig. 2. ^{1}H NMR spectrum at 300 MHz of the 1,4 aliphatic protons in polybutadiene.

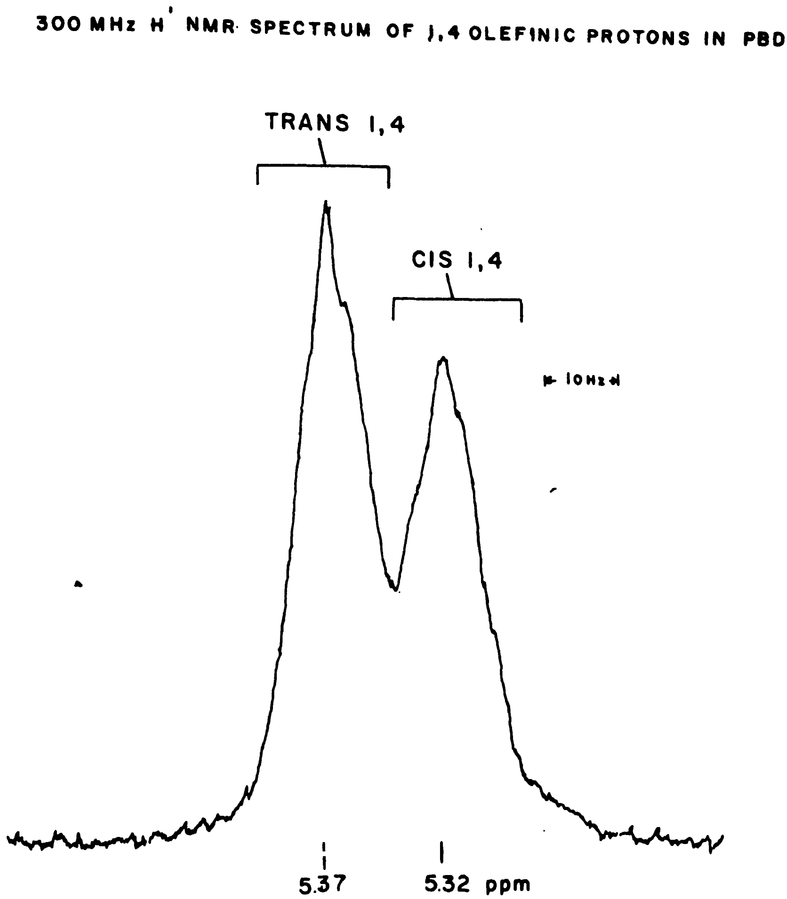

Fig. 3. [1]H NMR spectrum at 300 MHz of the 1,4 olefinic protons in polybutadiene.

a high trans (>90%) polymer indicates that these resonances represent the cis and trans contents of the polymer. Similarly, two resonances are observed for the olefinic cis-trans protons of 1,4 units (5.3 – 5.4 ppm) and their relative intensities are comparable to that of the methylene resonances.

To substantiate these assignments the spectrum of 4,8-dodecadiene was recorded. This material has been shown by ^{13}C NMR and IR spectroscopy (5) to be the cis-trans isomer. The olefinic proton resonances consist of two sets of peaks of equal amplitude as expected and which have chemical shifts similar to those of the polymer. The aliphatic region was not as distinct as the olefinic region due to spin-spin coupling effects.

Thus the cis-trans resonance peaks are believed to be defined as shown in Figure 1. Area measurements made in both the olefinic and aliphatic regions from a much narrower sweep width (250 Hz), shown in Figures 2 and 3, indi-

TABLE II

Comparison of cis/trans Mole Percent Isomeric Content Determined by Various Methods of Area Measurements

	Resonance Peaks			
	Aliphatic		Olefinic	
Method	Mole % Cis	Mole % Trans	Mole % Cis	Mole % Trans
Computer curve fitting	35	56	37	54
Electronic integration	45	49	39	52
Planimeter	45	49	39	52

cate a cis-trans ratio of 41/59 for this polymer. Since the polymer contains 91% 1,4 units it contains 37% and 54% cis and trans units, respectively. This compares favorably with IR results reported by Forman (6) for a polybutadiene prepared by BuLi initiation in hydrocarbon medium.

Since the peaks overlap somewhat, even at high temperature, several methods of curve decomposition were used. The results of the three methods, electronic integration, planimetry, and simulated curve fitting in both the aliphatic and olefinic regions are shown in Table II. All three methods yield consistent results when the olefinic region is studied. Cis-trans ratios estimated by fitting the aliphatic region also agree with these results.

The authors would like to thank Dr. V. Mochel for supplying 4,8-dodecadiene and L. Malotky for supplying the low vinyl polybutadiene.

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Received April 25, 1973
Revised June 25, 1973

PROTON NMR OF POLYBUTADIENE AT 300 MHz: cis-1,4-trans-1,4 LINKAGES

From ^{13}C NMR data, Mochel (1) concluded that there are no cis-trans linkages in polybutadienes polymerized by the n-butyllithium system. He proposed that at low vinyl contents (up to 20%) the vinyl units are isolated between blocks of cis-1,4 units and trans-1,4 units. At higher vinyl levels, blocks of vinyl units are observed. These conclusions were based upon the absence of separate peaks which might be attributed to the aliphatic carbons of a cis-trans linkage.

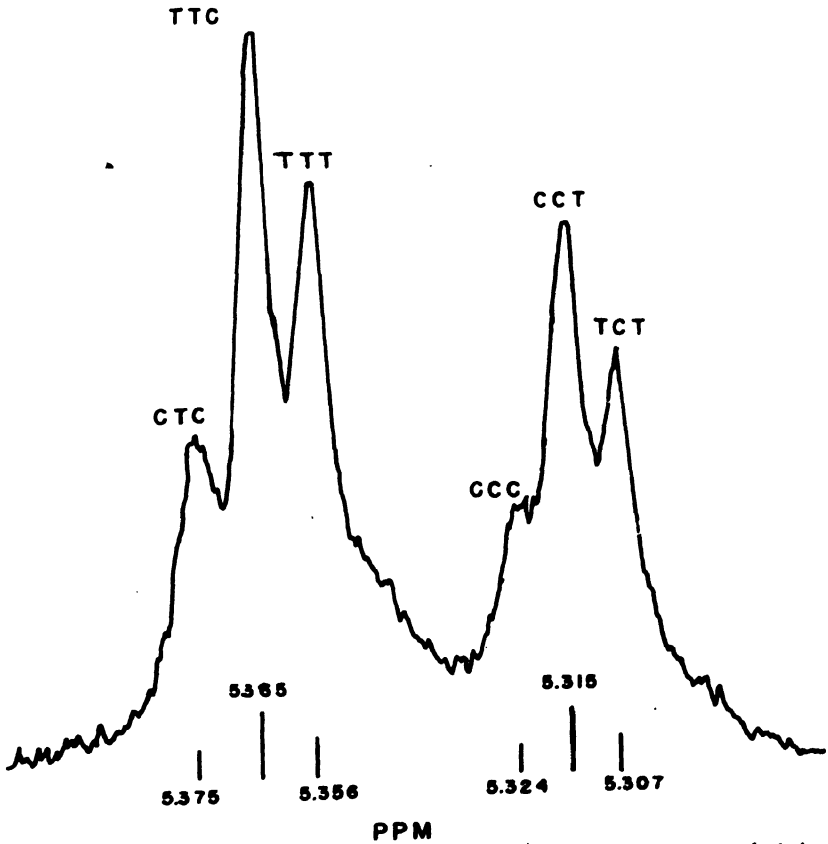

Fig. 1. cis-1,4 and trans-1,4 olefin resonance of polybutadiene with 1,4 methylene and vinyl methine protons decoupled. The six major peaks are assigned to isomeric triads as shown. Shift values are referenced to HMDS.

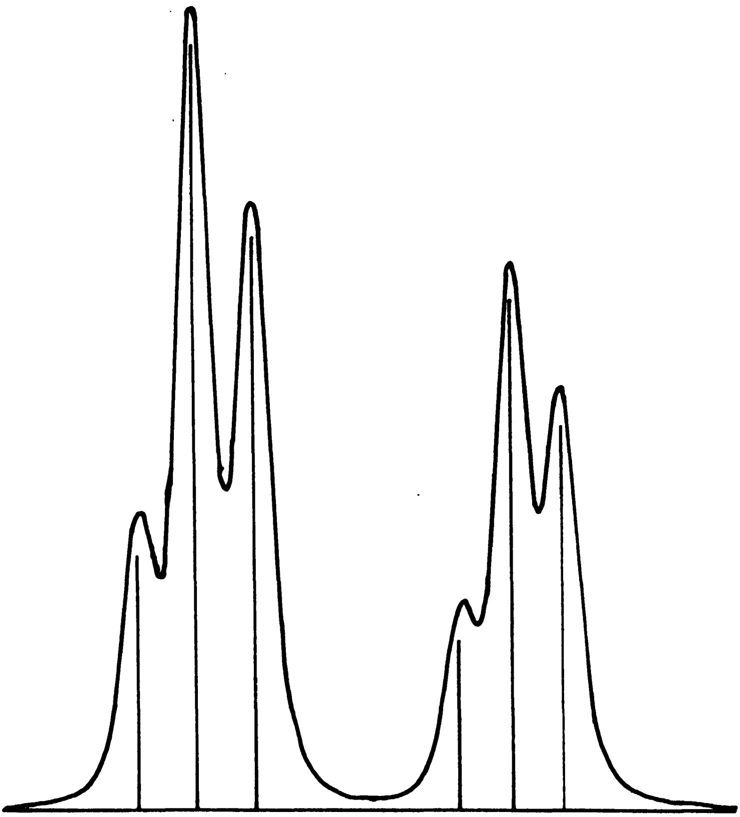

Fig. 2. Computer-simulation of the spectrum shown in Fig. 1 assuming a Bernoullian distribution of the cis-trans isomers.

With the use of ^1H high-resolution NMR at 300 MHz, there is now new spectroscopic evidence (2) which shows that there are cis-trans linkages, and furthermore, we have found that the distribution of cis and trans units can be determined and that it approximates that for Bernoullian statistics.

The complete spectrum of an n-butyllithium-catalyzed polybutadiene with a low vinyl content has already been shown (2). In that spectrum, the olefinic cis and trans proton peaks are clearly distinguishable at 5.32 and 5.37 ppm, respectively. The aliphatic region also shows the cis and trans peaks (2.03 and 1.98 ppm, respectively) quite well separated.

In this brief report we focus our attention on the cis and trans resonances of the olefinic region only. Figure 1 is the ^1H spin-decoupled spectrum of the cis and trans resonances on an expanded scale. In this figure the methylene resonances of the 1,4 units (and the methine resonance) are being irradiated, thus rendering the coupling with these protons unobservable. The vinyl protons are shifted out of the spectrum.

The six major peaks observed in the spectrum are essentially devoid of spin-

spin coupling and can be assigned to isomeric triads. This was confirmed by use of a series of polybutadienes of varying cis-trans content, prepared either by the isomerization of a high-cis polymer or by ring-opening polymerization of 1,5-cyclooctadiene. The six resonances are assigned as shown in Figure 1. The cis units are designated by c and the trans units by t. The peaks are assigned to the olefin protons of the central unit of the triads.

Figure 2 is a computer-simulated plot of the data obtained by assuming the assignment as shown and by assuming a Bernoullian distribution. Agreement is quite good. The additional resonance not accounted for by the six major peaks is attributed to triads involving a vinyl unit. Complete details will follow in a later publication.

From this evidence, we must conclude that the isomeric distribution is nearly random and that the earlier conclusion (1) that there are no cis-trans linkages in n-butyllithium polybutadienes is in error. We are also led to the conclusion that in ^{13}C NMR the methylene carbon peak positions of cis-trans linkages probably cannot be distinguished from those of cis-cis and trans-trans linkages with present day equipment. More evidence on this subject will be presented later.

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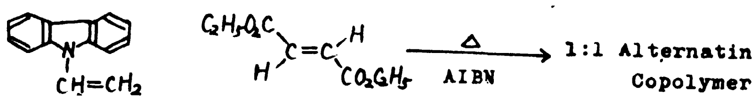
Received March 29, 1973
Revised June 25, 1973

MECHANISM OF CHARGE-TRANSFER POLYMERIZATION: FORMATION OF AN ALTERNATING COPOLYMER BETWEEN N-VINYLCARBAZOLE AND DIETHYL FUMARATE

The alternating copolymerization has been a subject of many reports in view of both synthetic and mechanistic interest. With regard to N-vinylcarbazole(VCZ), which has recently received much attention in the field of the polymerization initiated by an electron acceptor, only one example, i.e., VCZ-fumaronitrile(FN) system, has recently been reported by us (1). We wish to report here another new alternating copolymerization of VCZ with diethyl fumarate(DEF) as a comonomer, the rate features of which are quite different from those found for the VCZ-FN system.



N-Vinylcarbazole was purified as described before (2). Diethyl fumarate was first dried over calcium chloride and distilled twice over calcium hydride in vacuo under a nitrogen stream, bp, 75°C/5mmHg. Solution polymerizations were carried out in a sealed glass tube evacuated at 10^{-2} mmHg by means of several freeze-pump-thaw cycles. The polymerization system wrapped with aluminum foil to avoid exposure to light was allowed to stand in a thermostat maintained at 60 ± 0.1°C and 80 ± 0.1°C. The polymerization was stopped at low conversions, i.e., less than 10% at most. Polymers were precipitated with methanol, washed with it repeatedly, dried in vacuo and weighed. Reprecipitation of the polymer was made from benzene with methanol.

N-Vinylcarbazole was successfully copolymerized with DEF in a benzene solution under initiation with 2,2'-azobisisobutyronitrile (AIBN) to yield a 1:1 alternating copolymer regardless of the monomer feed ratio (3). The copolymer formation was confirmed by the solubility behaviors, elementary analyses, infrared, and ultraviolet spectra of the copolymers which were reprecipitated repeatedly. The copolymers were obtained as white powders softening between 180 and 210°C. The solubility behaviors are similar to those of VCZ homopolymer, but the copolymer is soluble in carbon tetrachloride in which VCZ homopolymer is almost insoluble. The infrared spectrum of the copolymer shows a strong carbonyl absorption at 1730 cm^{-1}. The absorption bands at 975 cm^{-1} and at 963 and 866 cm^{-1}, assigned to the trans out-of-plane =C–H deformation vibration in the DEF monomer and to the terminal vinyl group on a nitrogen atom in the VCZ monomer, respectively, essentially disappeared in the copolymer. It is indicated that the copolymerization proceeded at the

TABLE I

Compositions and Molecular Weights of the VCZ-DEF Copolymer

Mole fraction of VCZ in the monomer feed	N content in the copolymer (%)	Mole fraction of VCZ in the copolymer	Molecular Weight[a]
0.9	4.10	0.54	18,600
0.8	4.04	0.53	16,700
0.7	4.01	0.53	15,980
0.6	4.10	0.54	15,890
0.5	3.87	0.51	13,810
0.4	3.89	0.51	13,240
0.3	3.83	0.50	11,370
0.2	3.80	0.50	——
0.1	3.62	0.47	——

[a]Determined in benzene solution.

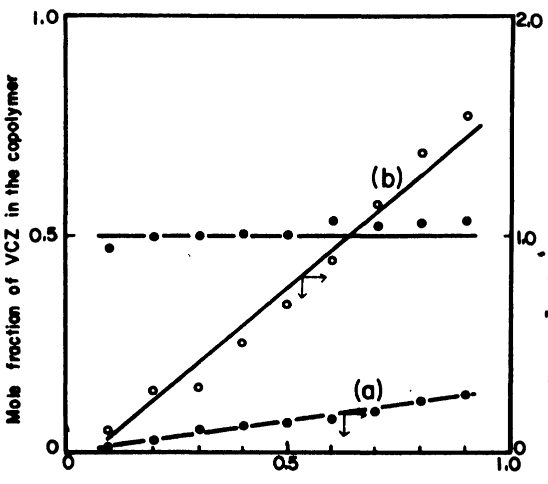


Fig. 1. Initial copolymerization rates vs. monomer feed ratios and copolymer compositions vs. monomer feed ratios. [VCZ] + [DEF] = 1.0 mole/l; [AIBN] = 1 × 10^{-3} mole/l; solvent, benzene; temp., 60°C (a), 80°C (b); polym. time, 30 min.

olefinic double bonds of both monomers. The number average molecular weights of the copolymers were greater than 10,000, increasing monotonously to 18,700 with the increase in the VCZ molar ratio in the monomer feeds as determined by the Mechrolab VPO. The results are summarized in Table I. Copolymer compositions were constantly 1:1, irrespective of widely varied

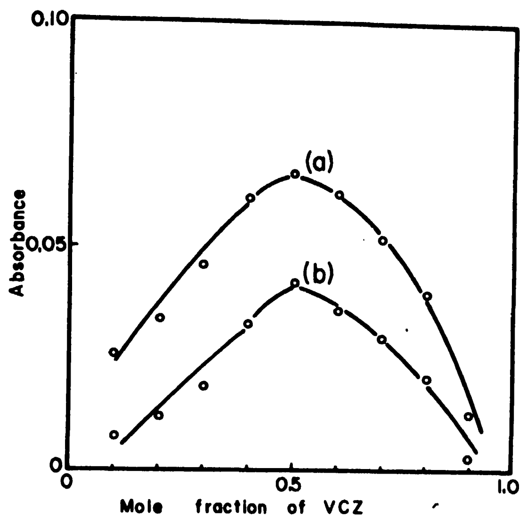


Fig. 2. Continuous variation method applied to the charge-transfer absorption in the VCZ-DEF system. [VCZ] + [DEF] = 0.1 mole/l; solvent, benzene; temp., 23°C. Measured at 370nm (a), and 380nm (b).

monomer feed ratios as determined from the nitrogen analysis (Figure 1, Table I). Thus the copolymer formed is assigned as the 1:1 alternating copolymer since the DEF monomer did not homopolymerize under the same conditions. Interestingly, the absorption spectrum of the copolymer is characteristic as found in the VCZ-FN 1:1 alternating copolymer. The $\pi-\pi^*$ absorption maxima due to the carbazyl moiety in the copolymer shifted to the blue region by about 5nm (λ_{max} = 338.5 and 325nm) as compared with those of the VCZ homopolymer (λ_{max} = 344 and 330nm). In the VCZ-FN alternating copolymer they are blue-shifted by about 10nm (1). When the initial copolymerization rate was plotted against monomer feed ratios, it increased steadily with the increase in the VCZ molar ratio in monomer feeds as shown in Figure 1. No maximum phenomenon of the rate was observed in the VCZ-DEF system, which is in striking contrast to the VCZ-FN system, where the rate maximum point was found at the molar ratio of 7:3 (VCZ:FN) under almost the same reaction conditions (1). It should also be noted that the polymerization rates of the VCZ-DEF system were approximately ten times slower than those of the VCZ-FN system.

The VCZ-DEF system shows very weak charge-transfer interaction in the ground state. Although no distinct charge-transfer band was observed, the absorption spectrum of the VCZ-DEF system shifted to the red region as compared with the sum of the absorptions of VCZ and DEF monomers of the same concentrations. Formation of the 1:1 charge-transfer complex in the ground state was confirmed by means of a continuous variation method applied to the absorption spectra (Fig. 2). It is expected that the more detailed

studies of these alternating radical copolymerization systems provide valuable information on the mechanism of the alternating radical copolymerization which still remains to be clarified. In addition, these new 1:1 alternating copolymers may serve as excellent model compounds for the study of the excimer state of poly-VCZ which has recently received attention (5,6).

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Received April 6, 1973
Revised May 22, 1973

SYNTHESIS OF 2-VINYLBENZIMIDAZOLE

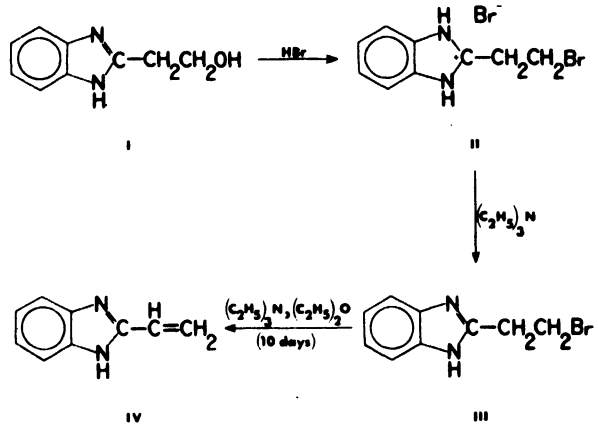
Attempts to synthesize 2-vinylbenzimidazole were made as early as 1949 when Bachman et al. (1) reported conventional dehydrohalogenation, dehydration, and pyrolysis procedures of the appropriate derivatives of 2-ethylbenzimidazole. These efforts produced only polymer. Subsequently in 1951, the synthesis of 2-vinylbenzimidazole by the spontaneous dehydrohalogenation of 2-β-chloroethylbenzimidazole in a moist atmosphere was patented (2). Characterization was not well done as only melting point determinations were made. In another patent report (3) which appeared in 1953, the same compound was prepared by the pyrolysis of α or β-acetoxyethylbenzimidazole to yield an oil which did not crystallize. Thereafter, a report on the synthesis appeared only in 1967, when Overberger et al. (4) prepared the monomer by the oxidative condensation of acrolein and o-phenylenediamine catalyzed by cupric acetate according to the general procedure described by Weidenhagen (5). They reported that the monomer, though produced in low yields (2%), is stable and could be purified by sublimation or recrystallization. It was properly characterized by its physical properties, element analysis, IR and NMR spectra.

This article presents a synthetic route which leads to a considerably higher yield of the monomer than previous routes. The starting material for the synthesis is 2-(β-hydroxyethyl)-benzimidazole whose preparation has been described by Bachman et al. (1) in detail. The synthesis, which is one of halogenation followed by dehydrohalogenation is outlined in Scheme 1.

Characterization of the monomer was done by melting point, IR, NMR, and elemental analysis. The mp is exactly the same as reported elsewhere (4), whereas the IR and NMR results presented here are more detailed compared to the earlier report (4). We note in this paper IR vinyl absorptions in addition to those at 925 and 980 cm^{-1} (4). Also, the NMR results presented here show finer structure compared to ref. (4), in that all vinyl peaks are quartets. The coupling constants and chemical shifts are characteristic of literature values for other vinyl groups (6).

Experimental

5.0 grams (0.03 mole) of 2-(β-hydroxyethyl)benzimidazole (purified twice by recrystallization from water, and vacuum dried) were placed in a pressure bottle having a glass stopper with a rubber gasket and clamps. To this were added 50 cc of concentrated hydrobromic acid (48% HBr), and after effecting a tight seal with the stopper the bottle was heated in a silicone oil bath at 145-150°C for 36 hr producing a yellowish-brown solution. The hydrobromic acid was then evaporated off using a rotary evaporator at 1 mm pressure and 70-80°C, to give a brown-colored solid. This solid was dissolved in a minimum



I 2-(β-hydroxy ethyl benzimidazole)

II 2-(β-bromo ethyl benzimidazole) hydrobromide

III 2-(β-bromo ethyl benzimidazole)

IV 2 vinyl benzimidazole

Scheme I

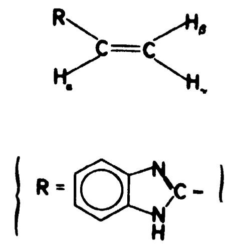
amount of absolute ethanol. A mixture of 250 cc of anhydrous ether and 40 cc of triethylamine (0.29 mole) was added, stirred for about 10 min, and the triethylammonium bromide salt was filtered off. An additional 10 cc of triethylamine and 50 cc of anhydrous ether were added to the filtrate and the solution was refrigerated at 0°C for 10-12 days in a stoppered conical flask. The mixture was then filtered to remove the solid (triethylammonium bromide) that had precipitated, and immediately evaporated at room temperature. A yellow crystalline solid was obtained which was stirred in a minimum amount of ethyl acetate (50 cc approx) to dissolve all soluble matter. The insoluble material (triethylammonium bromide salt) was filtered off and the filtrate was run through a chromatographic column packed with silica gel (chromatographic grade) and eluted with ethyl acetate. Liquid was collected till it no longer gave the characteristic deep blue color of the benzimidazole upon performing a TLC test, developing with ethyl acetate, and spraying with a 2% by weight solution of $CoCl_2 \cdot 6H_2O$ in ethanol (7). The clear liquid was then evaporated immediately at room temperature; the resulting pale yellow solid was vacuum dried and sublimed at 130°C and 200 μ vacuum to give a white solid, 2.5 g (60%), mp 187-189°C (lit. mp = 187-189°C (4)): IR(KBr) 925, 975, 990, 1310, 1430, 1450 cm^{-1} for vinyl absorptions; NMR(DMSO-d_6) τ 2.7 (m, aromatic), 3.2 (q, 1, α), 3.8 (q, 1, β), 4.4 (q, 1, γ) where α, β, γ are vinyl protons. The coupling constants are:

$J_{\alpha,\beta}$ = 16.5 Hz

$J_{\alpha,\gamma}$ = 10.0 Hz

$J_{\beta,\gamma}$ = 2.0 Hz

(see Scheme II).



Scheme II.

Anal Calcd for $C_9H_8N_2$: C, 75.0%; H, 5.6%; N, 19.4%. Found: .C, 74.70%; H, 5.75%; N, 19.04%.

Melting point was determined using a DuPont model 900 Differential Thermal Analyzer. The IR spectrum was obtained with a Perkin-Elmer model 521 spectrophotometer. The NMR spectrum was obtained with a Varian Associates model A-60 spectrometer. The elemental analysis was performed by Crobaugh Laboratories, Cleveland, Ohio.

The author gratefully acknowledges the financial support of the National Science Foundation under Grant No. GP-28264. He is also grateful to Dr. Morton H. Litt for his advice and stimulating discussions.

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Received November 15, 1972

SYNTHESIS AND POLYMERIZATION OF 2-VINYLIMIDAZOLE AND 2-VINYLBENZIMIDAZOLE

Our interest in well-defined monomeric and polymeric systems which contain the imidazole moiety arises primarily as a result of a continued interest (1) in the esterolytic activity of these systems. It was therefore desirable to develop procedures for the reproducible synthesis of isolable 2-vinylimidazole (1) and 2-vinylbenzimidazole (2) which could then be polymerized. Both 1 and 2 have been reported in the literature, however either their synthesis suffered from poor yields or the monomers polymerized so rapidly under the reaction conditions used that monomer isolation was difficult (3,4).

The general scheme used in this work involved the preparation and dehydrobromination of β-bromoethyl derivatives of the appropriate heterocyclic compounds. Previous attempts (2) to prepare these types of vinyl heterocyclic monomers by elimination of water, hydrohalogens, etc., led largely to polymeric materials. Condensation reactions using o-difunctional benzenes met with limited success in the preparation of 2-vinylbenzoxazole but failed in the synthesis of 2. We were interested in reaction conditions that not only affected dehydrobromination but which also did not cause the monomeric vinylic products to react further.

It was found that a spontaneous dehydrobromination of 2-β-bromoethylimidazole (3), and 2-β-bromoethylbenzimidazole (4) in the solid state (3) and subsequent treatment of the resulting hydrobromide salts with aqueous potassium carbonate solutions afforded 1 and 2, respectively, in good yields. A similar synthesis of 2 in 60% yield is reported in this same issue of the "Journal" by N. G. Kumar (5). Polymerization and copolymerization reactions of these monomers were also studied.

Results

A new procedure for the preparation of 1 is described in this paper. Compound 1 had been previously prepared by the dehydration of 2-β-hydroxyethylimidazole (4), (5) in an 11.9% yield. The procedure used for the preparation of 5 was from the patent literature (3). Treatment of 5 with concentrated hydrobromic acid gave an 88% yield of 2-β-bromoethylimidazole hydrobromide (6). Compound 6 was neutralized with triethylamine to give 2-β-bromoethylimidazole (3) which was converted to 2-vinylimidazole hydrobromide (7) by exposure to the atmosphere at room temperature. Workup of 7 afforded a 94% yield of 1 and an overall yield from 5 to 1 of 83%.

This method was then extended to a preparation of 2-vinylbenzimidazole (2). A series (2) of elimination reactions of α- and β-substituted 2-ethylbenzimidazole compounds failed to yield desired monomeric products. Reports in the

patent literature (3a) indicate the preparation of 2 by spontaneous dehydrohalogenation of 2-β-chloroethylbenzimidazole but the reactions and products were not well-defined.

A 70% conversion of 2-β-ethoxyethylbenzimidazole (8) to 2-β-bromoethylbenzimidazole hydrobromide (9) was effected by heating 8 with concentrated hydrobromic acid (2). The addition of 9 in methanol to triethylamine in ether resulted in a 98% yield of 4. When 4 was placed in a dessicator for five days it formed 2-vinylbenzimidazole hydrobromide 10 in the solid state which was treated with base to afford 2. The melting point of 2 was dependent upon the heating rate since a bulk polymerization occurred below the melting point. Slower heating resulted in more polymer and a higher apparent melting point. The dehydrohalogenation reaction in this case was not as reproducible as that for the preparation of 1. The purity of the starting material influenced the yield and purity of the product as did a thinner layer of crystals on the wall of the flask during the dehydrohalogenation. It was not determined just how the reaction depended on the presence of water in this layer of crystals. The overall yield for the two-step conversion of 8 to 2 was about 33%.

2-Vinylimidazole was homopolymerized by a radical initiator both in methanol and in toluene. During the polymerization in toluene the polymer which precipitated was always discolored. The intrinsic viscosities of these polymers were approximately 0.4. Monomers 1 and 2 were both subjected to ^{60}Co irradiation. If the monomers had been recrystallized after sublimation, then 1 afforded crosslinked polymer while 2 gave a linear polymer. If they were not recrystallized, then the irradiated samples became discolored but did not polymerize.

Experimental

2-β-Hydroxyethylimidazole (5)

This compound was prepared following the procedure described by Lawson (4).

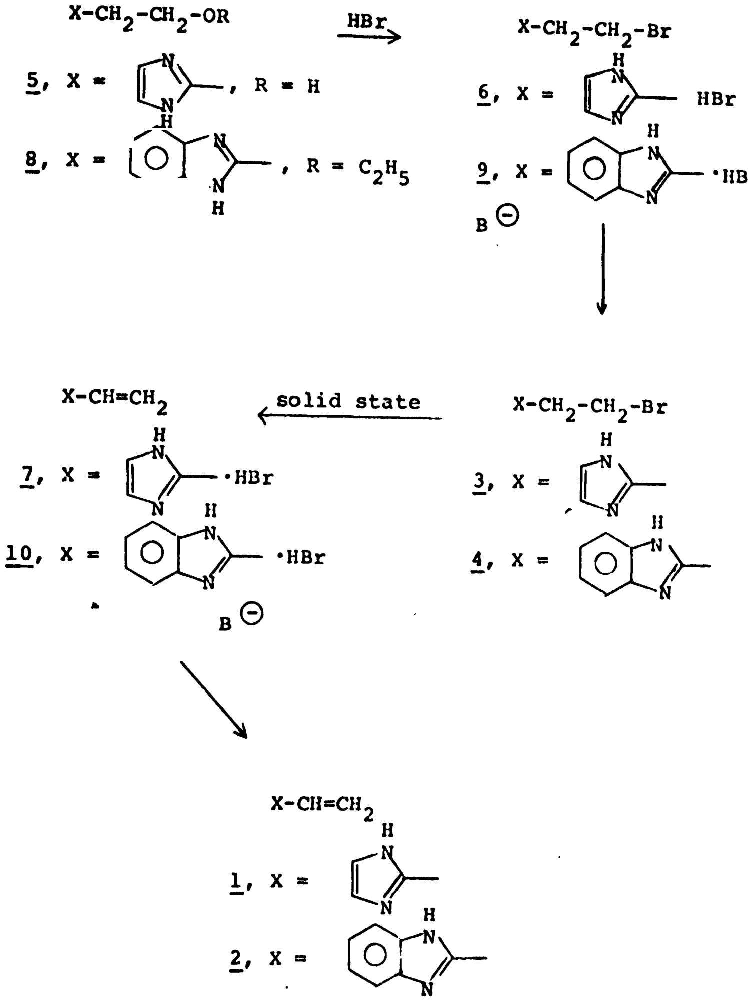
2-β-Bromoethylimidazole Hydrobromide (6)

A solution of 4.94 g (0.043 mole) of 5 in 25 ml of concentrated hydrobromic acid was heated to about 140°C. The hydrogen bromide was allowed to evaporate and the pressure was reduced to remove the volatile impurities. This procedure was repeated. The residue which solidified was recrystallized from acetone to afford 7.1 g of an almost white salt. An additional 2.9 g of a slightly colored salt was obtained from the mother liquor to give an overall yield of 88%. After additional recrystallization the mp was 132-133°C.

Anal. Calcd for $C_5H_8Br_2N_2$: C, 23.46%; H, 3.15%; N, 10.95%; Br, 62.44%. Found: C, 23.61%; H, 3.07%; N, 11.10%; Br, 62.47%.

2-Vinylimidazole (2)

To a stirred solution of 70 ml of ether and 70 ml of triethylamine was added 3.76 g (0.0147 mole) of 2-β-bromoethylimidazole hydrobromide, (6) in 8 ml of ethanol. The precipitate that formed was removed by filtration and



Scheme I

washed twice with 20 ml of ether to yield 2.62 g (ca. 100%) of triethylamine hydrobromide. The ether layers were combined, dried, and the solvent was removed to yield 2.56 g (0.0146 mole) of the crystalline hydrobromide (3).

The 2-β-bromoethylimidazole hydrobromide crystals were kept under reduced pressure for 4 hr. After 2 hr the crystals had completely changed shape and after 4 hr had become a liquid. To this liquid was added 3 ml of concentrated potassium carbonate solution and was extracted 3 times with 50 ml of ether. The combined ether solutions were dried with $MgSO_4$, filtered, and the ether evaporated to leave 1.86 g of an almost white, low melting solid. After an additional 18 hr, the residue was subjected to treatment by another 3 ml of potassium carbonate solution and the same extraction procedure to afford

1.30 g (0.0138 mole) of solid 2. The yield was 94.5%. Sublimation at 30°C (0.0005-0.001 mmHg) gave a solid with a mp of 130°C.

Anal. Calcd for $C_5H_6N_2$: C, 63.81%; H, 6.43; N, 29.76. Found: C, 63.65; H, 6.46; N, 29.63.

2-β-Ethoxyethylbenzimidazole (8)

Compound 8 was prepared by a known procedure (2).

2-β-Bromoethylbenzimidazole Hydro Bromide (9)

2-β-Ethoxyethylbenzimidazole, (8), (2.1 g, 0.011 mole), was treated with 25 ml of concentrated hydrobromic acid for 4 hr at 150°C during which time the volatiles were removed under a slightly reduced pressure. Recrystallization from isopropanol-acetone gave 2.3 g (68%) of 9. After recrystallization the mp was 193-195°C.

Anal. Calcd for $C_9H_{10}Br_2N_2$: C, 35.35%; H, 3.29%; Br, 52.17%; N, 9.17%. Found: C, 35.49%; H, 3.32%; Br, 52.21%; N, 9.19%.

2-β-Bromoethylbenzimidazole (4)

A solution of 1.61 g (0.00526 mole) of 9 in 11 ml of ethanol was added to a stirred solution of 6.2 ml of triethylamine in 50 ml of ether. The precipitate which formed was removed by filtration and washed with ether to give 0.941 g (98.5%) of triethylamine hydrobromide. Combination of the ether solutions and evaporation of the solvent afforded 1.158 g (98%) of 4 as a white solid which was recrystallized from water. Heating showed a transition at 70-80°C after which the material was stable up to a temperature of 235°C. The reaction was followed by infrared spectroscopy which indicated that the reaction was complete after 3 hr.

Anal. Calcd for $C_9H_9BrN_2$: C, 48.02%; H, 4.03%; Br, 35.50%; N, 12.45%. Found: C, 47.77%; H, 4.19%; Br, 35.44%; N, 12.40%.

2-Vinylbenzimidazole (2)

Solid 2-β-bromoethylbenzimidazole, (4), (1.115 g; 0.00495 mole) was allowed to react in a dessicator for 5 days. The product, 10, was then dissolved in 10 ml of ethanol and added to a solution of 5 ml of triethylamine in 50 ml of ether which afforded a precipitate that was filtered to yield 0.53 g (60%) of triethylamine hydrobromide. Evaporation of the ether left 0.993 g of 2 which was allowed to stand in the dessicator for one additional day at which time this material was treated with a mixture of ether and an aqueous potassium carbonate solution. Evaporation of the 250 ml of ether left a residue of 0.359 g (49%) of crude 2 with a mp of 176-179°C. Purification was effected by sublimation at 0.001 mm at 110°C to give 2 with a mp of 187-189°C (lit. (5,6) 187-189°C) with high heating rates. With slow heating rates a reaction (solid-state polymerization) occurred at 170-180°C with no melting up to 250°C.

Polymerization of 2-Vinylimidazole

a) In Toluene. 2-Vinylimidazole (0.305 g) and AIBN (0.006 g) were dissolved in 40 ml of toluene and placed under nitrogen. The solution was heated to 60°C and an additional 0.006 g AIBN was added after 48 hr and again after 72 hr. The solvent was evaporated from the final turbid solution,

the residue dissolved in dilute hydrochloric acid and dialyzed for 14 days. Freeze-drying afforded 0.0803 g of poly-2-vinylimidazole, $[\eta] = 0.37$.

Anal. Calcd for $(C_5H_6N_2)_x$: C, 63.81%; H, 6.43%; N, 29.76%. Found: C, 55.81%; H, 5.83%; N, 26.66%.

b) In Methanol. 2-Vinylimidazole (0.396 g) and AIBN (0.085 g) were dissolved in 7 ml of dry methanol, degassed, and sealed in a tube. The solution was heated at 50°C for 4 days. The colorless solution was added to 200 ml of acetone which precipitated 0.1347 g of white polymer. The polymer was further purified by passage of a methanol solution over a Sephadex LH-20 gel permeation column to yield 0.1162 g, $[\eta] = 0.41$.

Anal. Calcd for $(C_5H_6N_2)_x$: C, 63.81%; H, 6.43%; N, 29.76%. Found: C, 61.46%; H, 6.73%; N, 28.88%.

The intrinsic viscosities were measured at 25°C in methanol with a Ubbelohde viscometer.

Radiation induced Polymerization of 2-Vinylimidazole and 2-Vinylbenzimidazole

Solid 2-vinylimidazole or 2-vinylbenzimidazole (ca. 0.5 g) was sealed under nitrogen and kept at 0°C for 24 hr during which time the samples received a calculated dosage of 10^6 rad from a ^{60}Co source. Examination of the resulting solids showed that vinyl polymers were formed in both cases. The poly (2-vinylimidazole) was crosslinked.

The authors are grateful for financial support of the National Institutes of Health under Grant No. 2 RO1 GM 15256.

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Received June 22, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 471-477 (1973)

THE KINETICS OF FREE RADICAL POLYMERIZATION OF VINYLFERROCENE

Introduction

Vinylferrocene has been shown (1-4) to form homopolymers and copolymers quite readily. Only one kinetic study has been reported (5) which suggested that vinylferrocene polymerized according to established vinyl polymerization mechanisms (6). However, a recent kinetic study conducted in these laboratories on the homopolymerization of this monomer has indicated that vinylferrocene does not follow normal vinyl polymerization mechanisms. Thus the initial rate of polymerization at low conversions was found to be dependent on the initial monomer concentration, $[M]_0$, to a power $1 \cdot 12$ and on the initial initiator concentration, $[In]_0$, to a power $1 \cdot 11$.

This result suggests that the termination reaction is both monomolecular and intramolecular. A kinetic scheme is proposed which satisfies the experimental data. Implicit in this scheme is the suggestion that the polymer contains unpaired electrons. The presence of unpaired electrons in polyvinylferrocene has been indicated by nmr and Mössbauer spectroscopy and confirmed by esr spectroscopy.

It is considered that the termination reaction involves direct participation, possibly with solvent interaction, of the ferrocene nucleus. In this reaction an electron is transferred from the iron atom to the growing polymer chain radical and the chain radical becomes deactivated. The resultant paramagnetic species produced in the polymer molecule is considered, on the basis of spectral evidence, to be a transition metal complex in which the iron is formally in the Fe(III) state.

Experimental

Vinylferrocene was purified by successive sublimations at 30°C and 0.1 mm Hg (mpt 52.5 to 53.5°C). Gas chromatography (Pye Unicam 101, carbowax column at 150°C) confirmed a pure sample. 2,2′-azobisisobutyronitrile (AIBN) was recrystallized three times from AnalaR methanol (mpt 101°C to 102°C with decomposition). AnalaR benzene was refluxed over phosphorus pentoxide for six hours and then distilled from fresh phosphorus pentoxide and the middle fraction collected. Rates of polymerization were determined by dilatometry (7) after degassing the reactants by three freeze-thaw cycles at 10^{-4} mm Hg. The density and apparent density of the monomer and polymer were determined by the method of Matheson et al. (8) modified to a small scale. Polymerizations were allowed to proceed to ca. 5% conversion and then the reaction was stopped by precipitation into methanol containing a trace of

TABLE I

Homopolymerization of Vinylferrocene in Benzene Initiated by AIBN

T°C ±0.01	$[M]_0$ mole dm^{-3}	$[In]_0 \times 10^2$ mole dm^{-3}	Conversion %	$Rp \times 10^5$ mole dm^{-3} s^{-1}	$\left\{\frac{Rp \times 10^4}{[M]_0^{1.12}\ [In]_0^{1.11}}\right\}$	$\bar{M}_n$*
60	4	0.4	0.6	0.54	5.1	5,900
60	4	1.0	1.8	1.62	5.4	–
60	4	1.0	1.8	1.67	5.6	5,600
60	4	1.8	3.1	2.90	5.0	6,800
60	4	2.0	3.2	3.21	5.1	7,900
60	1	1.0	1.1	0.42	6.0	–
60	2	1.0	1.6	0.78	5.9	2,700
60	3	1.0	1.9	1.34	6.4	5,800
60	4	1.0	1.8	1.71	5.9	6,300
60	4	0.4	0.9	0.58	5.7	–
70	4	0.4	2.0	3.35	–	3,400
75	4	0.4	3.8	5.87	–	6,900
80	4	0.4	5.8	9.54	–	6,600

*Number average molecular weight determined in benzene solution at 37°C by vapor pressure osmometry.

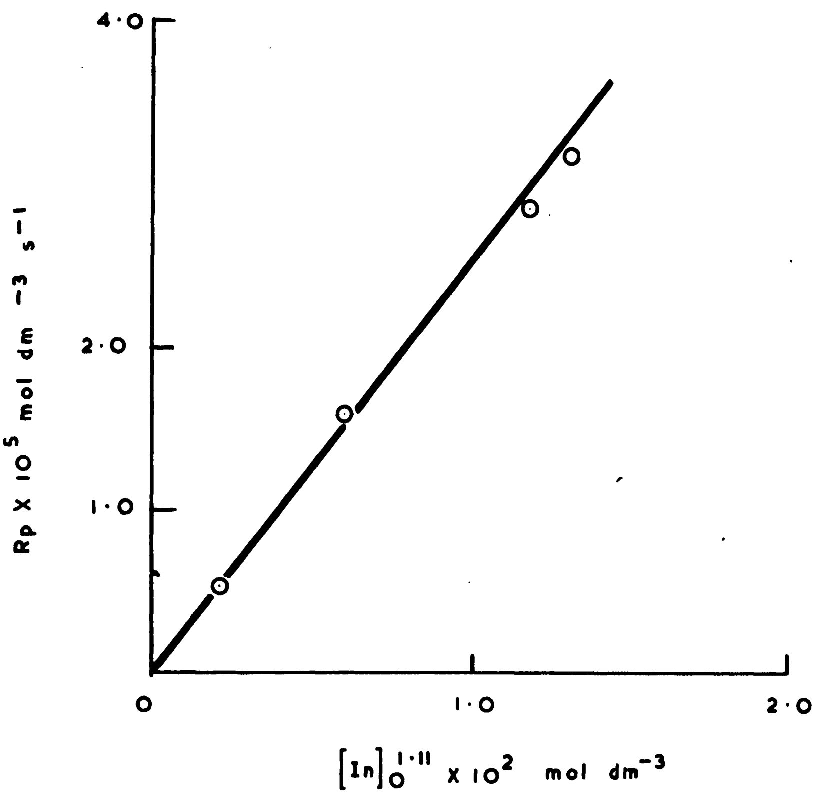


Fig. 1. Initial rate of polymerization of vinyl ferrocene in benzene at 60°C as a function of $[In]_0^{1.11}$ at constant $[M]_0$. $[M]_0$ = 4.00 mole dm^{-3}.

hydroquinone. The polymer was redissolved in benzene, precipitated into methanol, and collected on a sintered glass crucible and dried to constant weight at 60°C and 0.1 mm Hg.

Results and Discussion

Representative results of the kinetic experiments are summarized in Table I. Logarithmic plots, using the least squares method of the initial rate of polymerization against initial monomer and initiator concentrations, gave straight lines with slopes equal to 1.12 and 1.11 respectively. The rate expression is therefore of the following form:—

$$R_p = k[M]_0^{1.12}\ [In]_0^{1.11} \tag{1}$$

where k = 5.6 X 10^{-4} when R_p is expressed in mole dm^{-3} s^{-1} and $[M]_0$, $[In]_0$

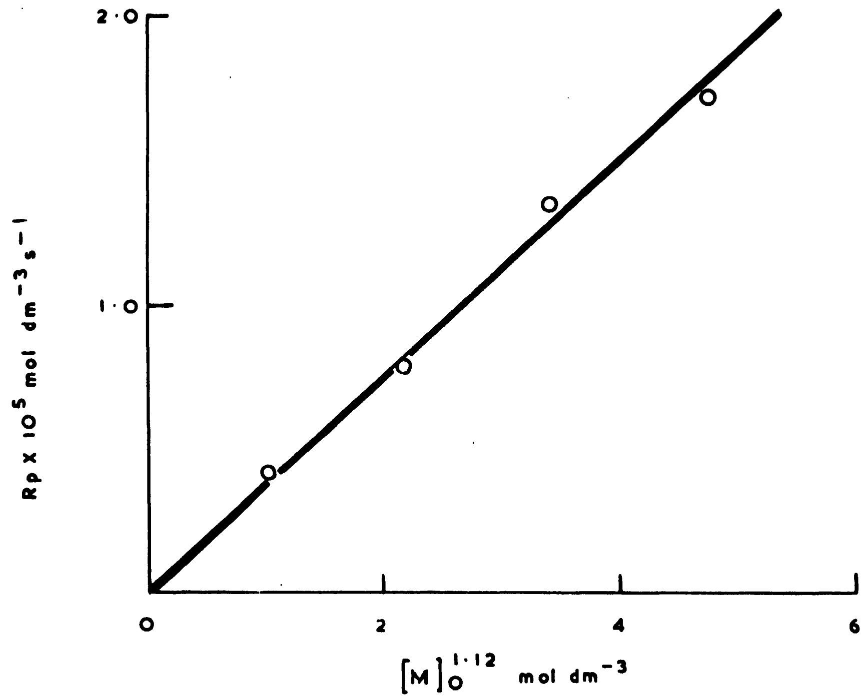


Fig. 2. Initial rate of polymerization of vinyl ferrocene is benzene at 60°C as a function of $[M]_0^{1.12}$ at constant $[In]_0$. $[In]_0 = 1.0 \times 10^{-2}$ mole dm^{-3}.

in mole dm^{-3}. Plots of R_p against $[M]_0^{1.12}$ and $[In]_0^{1.11}$ are shown in Figures 1 and 2 respectively. The overall activation energy for the polymerization between 60°C and 80°C was found to be 139.7 kJ mole^{-1}.

The dependence of the rate on the initiator concentration to a power of approximately 1.0 indicates that the predominant termination step is monomolecular. Normally the termination step in vinyl polymerizations is bimolecular and involves a mutual reaction between two polymer chain radicals (6). Furthermore, the overall form of the rate expression suggests that the termination reaction is intramolecular and does not involve hydrogen abstraction from monomer as in the case of allylic polymerizations (9).

The rate expression can be explained if the termination reaction involves only one growing polymer radical and the product of this reaction is inactive. In accordance with accepted practice (6), the following kinetic scheme can be suggested:

Initiation: $In \longrightarrow 2R_c^{\bullet}$ velocity constant k_d

$R_c^{\bullet} + M \longrightarrow R_1^{\bullet}$ velocity constant k_i

Rate of initiation: $I = 2k_d f[In]$ (2)

where f is the initiator efficiency and [In] represents the initiator concentration.

Propagation: $R_n^{\bullet} + M \longrightarrow R_{n+1}^{\bullet}$ velocity constant k_p

Rate of monomer removal $= -d[M]/dt = k_p[M][R\cdot]$ (3)

where $[R\cdot] = \sum_{i=1}^{i=\infty} [R_i^{\bullet}]$ = total concentration of polymer radicals.

Termination: $R\cdot \longrightarrow$ inactive species, velocity constant k_t. Making the steady state approximation,

$$[R\cdot] = \{2k_d f[In]/k_t\} \quad (4)$$

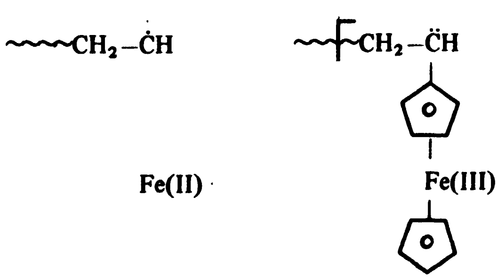
whence the rate of polymerization =

$$R_p = -d[M]/dt = k[M][In] \quad (5)$$

where k is a composite constant equal to $\{2k_d f k_p/k_t\}$

This scheme is in reasonable agreement with the experimental results summarized in eq. (1). The relatively high activation energy is also in agreement with this kinetic scheme.

Two characteristic features of metallocenes are their ready oxidation to cationic species by loss of one or more electrons from the metal atom (10) and direct participation of the metal atom in many reactions (11). It seems probable, therefore, that the termination step involves an electron transfer from the iron atom to the polymer chain radical which deactivates the radical and leaves an unpaired electron in the ferrocene nucleus. The ferrocene nucleus which loses an electron in the termination reaction does not retain its d^5 low spin configuration, and evidence presented below suggests that rearrangement occurs to form a polymer molecule containing an Fe(III) high spin complex. A tentative reaction could be depicted:



polymer molecule containing Fe(III) high spin complex

Thus, the proposed mechanism for the termination step implies that each polymer molecule produced in this reaction contains unpaired electrons. This

observation is supported by spectral studies. The nuclear magnetic resonance (nmr) spectra showed pronounced paramagnetic broadening which was independent of temperature. Paramagnetic broadening of the nmr spectra of addition polymers containing ferrocene has recently been reported (12) and the effect was still present after the addition of ascorbic acid. This suggests that the ferricenium cation was not present. The Mössbauer spectra of polymer samples contained a significant third peak at a small positive velocity (0.17 mm/s) which was not present in the monomer. The peak is not consistent with the ferricenium cation, but appears more likely to be an ionically bound complex involving Fe(III) high spin. This observation is supported by the temperature dependence of this peak which is reduced at low temperatures. Peaks due to covalently bonded iron tend to increase with decreasing temperature. The area of the third peak in the Mössbauer spectra varies between 3% to 14% of the total area and depends on the molecular weight of the polymer and on the extent of conversion of monomer to polymer. The electron spin resonance (esr) spectra confirmed the presence of a substantial concentration of a paramagnetic component in the polymer molecules. A single broad line was observed from solutions in benzene and from the solid polymer. The width varied from 425 gauss in benzene solution to 600 gauss in the solid state at room temperature. At liquid nitrogen temperature the solid produced a line width of 850 gauss. The 'g' value obtained for the centre of the peak was 2.06. The measured spin concentration was necessarily imprecise as it was obtained by comparison of the rather broad peaks with the narrow line from chromium in magnesium oxide. However the recorded value of 10^{19} spins/gram is consistent with the concept of one paramagnetic species per molecule (a value of 8.5×10^{18} spins/gram would correspond to one spin per molecule for a number average molecular weight of ca. 7000). The spectra are consistent with Fe(III) in a high spin configuration which support the Mössbauer results.

Since ferrocene and its compounds are generally regarded as being stable to atmospheric oxidation (13), it is unlikely that oxidation of ferrocene nuclei in polyvinylferrocene is the cause of the spectral results. If oxidation takes place upon storage, then the esr signals should increase with time. This has not been observed. Likewise, oxidation during the polymer isolation is unlikely because Mössbauer studies indicate that the percent of paramagnetic species varies systematically with the degree of polymerization of the polymer examined.

Thus the spectral observations are in agreement with the kinetic analysis. On the basis of spectral evidence it is considered that after the initial electron transfer reaction which terminates the growing polymer chain, a polymer molecule is produced which contains a metal complex of iron in a Fe(III) high spin configuration.

Further studies are in progress to elucidate the precise mechanism operating in the termination step and to characterize the paramagnetic species and its position in the polymer.

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Revised May 15, 1973

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COPOLYMERIZATION OF CARBON DIOXIDE AND N-PHENYLETHYLENEIMINE

Carbon dioxide had long been regarded as an inert material for synthesizing high polymer until Inoue et al. (1) succeeded in producing alternate copolymers with epoxide.

In this communication, we wish to report the synthesis of polyurethane from carbon dioxide and N-phenylethyleneimine in the presence of some organometallic compounds.

A 30-ml stainless autoclave was degassed in vacuo and cooled at −78°C. Measured amounts of the catalyst and N-phenylethyleneimine were placed in it, and then carbon dioxide was introduced. The vessel was kept standing in an oil bath for 10 hours at 80°C. The white polymer produced was washed with diethyl ether and ethanol and then dried in vacuo at room temperature overnight.

In Figure 1 are shown the typical infrared spectra of the polymers, which show the characteristic absorption band of urethane linkage at about 1735 cm^{-1} (Run no. 3). Results of copolymerization with various catalyst systems are summarized in Table I.

From these results, it can be said that some organometallic compounds such as titanium tetra-n-butoxide, aluminum n-butoxide, and so on are effective catalysts for producing polyurethane from carbon dioxide and N-phenylethylene-

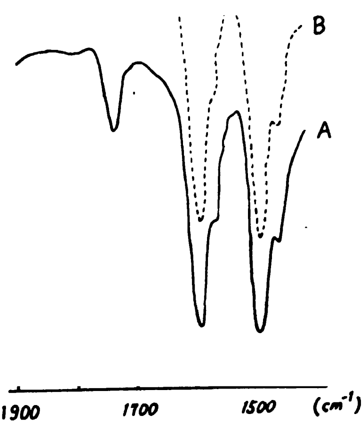

Fig. 1. Infrared spectra of carbon dioxide-N-phenylethyleneimine copolymer (Run no. 3) (A) and poly-N-phenylethyleneimine (Run no. 2) (B).

imine. Polyurethane was also produced with the use of propylene imine and carbon dioxide in the presence of these catalysts.

The precise study is now in progress.

TABLE I

Copolymerization of Carbon Dioxide with N-phenylethyleneimine. (Polymerizations were Carried Out at 80°C for 10 Hours with the Use of 0.30 g of N-phenylethyleneimine, 10 g of Carbon Dioxide, and 0.01 g of Catalyst).

Run no.	Catalyst	Polymer yield (g)	Absorption at 1735 cm^{-1}	η_{sp}/C [a]	Elemental analysis
1	none				
2	$BF_3(C_2H_5)_2O$	0.20	-	0.13	C, 80.70; N, 11.71; H, 7.53 Ash, 0.00
3	$Ti(OC_4H_9)_4$	0.20	+	0.11	C, 71.30; N, 9.87; H, 7.33 Ash, 0.65 (0, 10.87)
4	$Al(OC_4H_9)_3$	0.27	+	0.10	C, 72.53; N, 9.93; H, 7.47 Ash, 0.00 (0, 10.07)
5	$ZnCl_2$	0.12	+		

[a] The specific viscosities of 0.25 % solution of 90 % formic acid at 25°C

[b] Calcd. for N-phenylethyleneimine (C_8H_9N): C, 80.62, N; 11.76; H, 7.63

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Received May 7, 1973
Revised June 11, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 481–484 (1973)

THE EFFECT OF THE DISTRIBUTION OF COLORANT ON THE COLOR OF FIBERS*

In a recent note, Allen and Goldfinger (1) have shown that for an optically and geometrically simple case, the effect of "ringdyeing" on the color of fibers can be calculated by extending the general treatment of the prediction of the color of absorbing-scattering substrates (2).

"Vylor" nylon monofilament Type 0200 SA, 330 denier (0.22 mm diam) was dyed with Azo Phloxine GA Ex. Conc. (C. I. Acid Red 1, C. I. #18050) at 95°C for 30 min.

At the high dye concentrations and low pH used in this work; i.e., 1 g of dye per liter of solution, 0.3 g of dye per g of fiber in formic acid solution at pH 3.2, the dye does not obey Fick's law in diffusing into the fiber. For most of the depth of penetration, the dye concentration is approximately constant then decaying very sharply to low values and then approaching zero asymptotically. The depth of penetration is of course proportional to the square root of the dyeing time (3) (Fig. 1).

Further treatment of the filaments at 95°C in formic acid at pH 3.2 for 50 hr resulted in the close to uniform redistribution of the dye.

Colorimetric determination of the relative dye concentration before and after the redistribution showed a fractional decrease of the concentration by 0.054 ± 0.0013 as a result of this treatment.

Simultaneously, fibers were exposed to the same conditions as those fibers which were dyed, except for the presence of the dye. Thus two pairs of samples with identical history were available, one of the first pair being ringdyed and one of the second pair having its dye almost uniformly distributed. Reflectance curves against corresponding undyed fibers were measured on a Hardy spectrophotometer (Fig. 2).

For the reflectance measurements, the fibers were assembled in parallel bundles behind glass plates. These bundles were sufficiently thick (approximately 16 layers) so that the reflectance of the background had no measurable effect.

The results are presented in Figures 3 and 4. In Figure 3, the ratio of the reflectances of the ringdyed sample to that of the uniformly dyed sample (corrected for the dye loss) is plotted against CK (1,2) a linear function of the exponent in the Beer-Lambert equation.

In Figure 4 the same ratio is shown plotted against the reflectance of the sample in which the dye is uniformly distributed. In addition to the ratio predicted by Allen and Goldfinger, predictions based on the Kubelka-Munk treatment are shown.

*This paper was presented at the Twelfth Sesqui-Annual Symposium on Polymer and Fiber Microscopy on May 11, 1973 at Raleigh, N.C. Sponsored by the Textile Research Institute, Princeton, New Jersey.

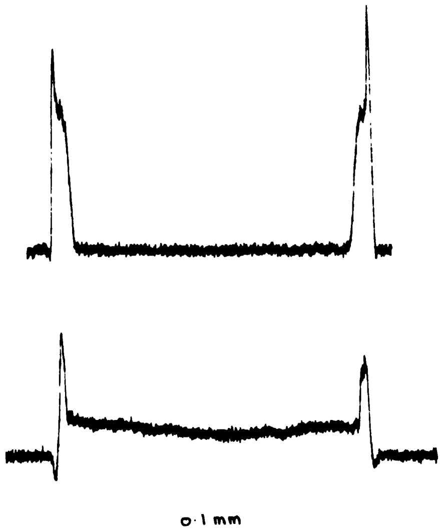

Fig. 1. Densitometer tracing, top: ringdyed fiber; bottom: fiber with dye redistributed. On the bottom tracing the Becke line can be clearly identified. Its breadth at the bottom is subtracted from the breadth of the ring (top tracing). This difference is assumed to be the true thickness of the ring.

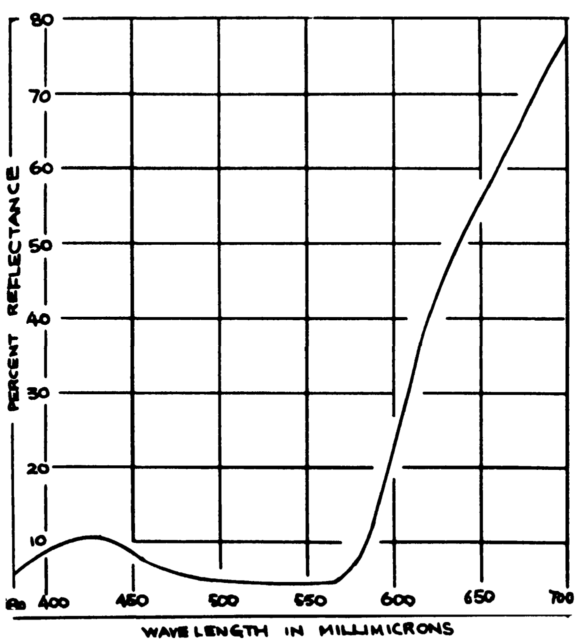

Fig. 2. Reflectance spectrum of parallel bundle of dyed fibers measured against a similar bundle of undyed fibers.

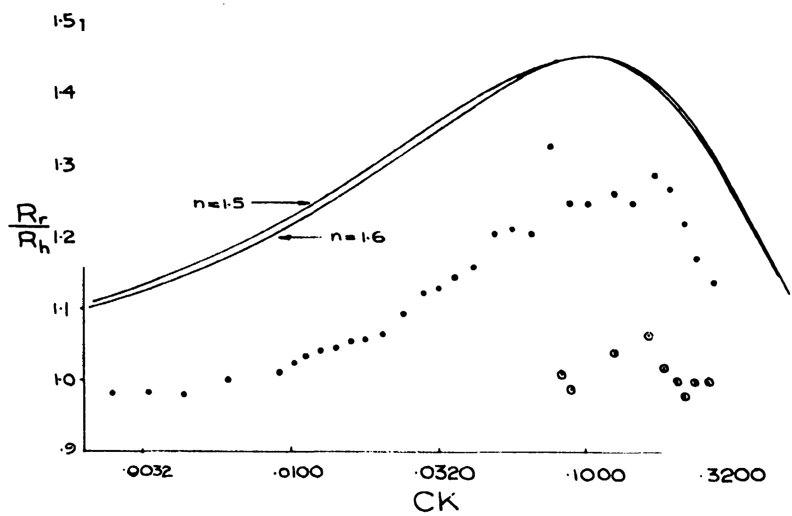

Fig. 3. Effect of ringform distribution of dye on the color of fiber bundles. The ratio of the reflectance of the ringdyed fiber bundle to that of uniformly dyed fiber of equal dye concentration R_r/R_h plotted against CK, the exponent of the Beer-Lambert equation. The continuous lines are the values predicted by Allen and Goldfinger. The circled points correspond to reflectance values obtained between 0.38 and 0.52 microns. In that wavelength range the fibers discolor significantly.

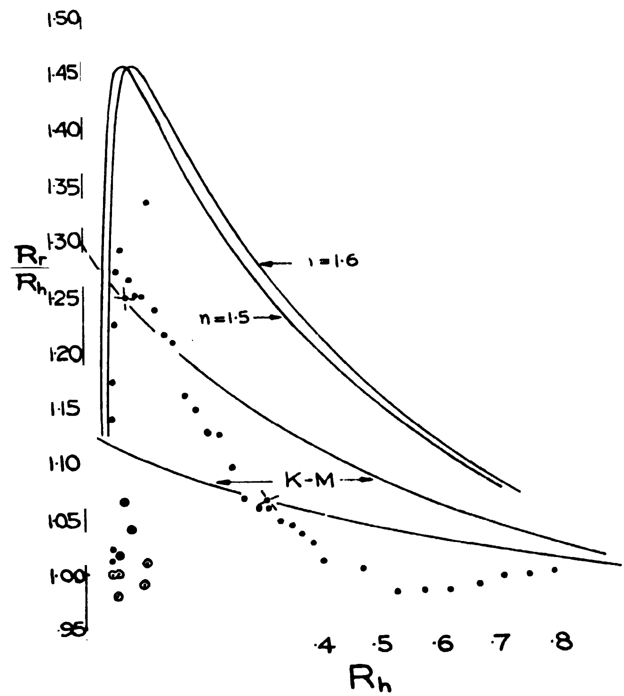

Fig. 4. Same values of R_r/R_h as in Fig. 3 plotted against R_h. The two curves marked K-M were calculated from the Kubelka-Munk relationship, taking the starred points as the basic K/S values and calculating reflectance ratios from their corresponding multiples and fractions.

Obviously in the wavelength range in which no light is absorbed the distribution of the (ineffective) dye can have no effect and the reflectance ratio must be one. If all of the refracted light is absorbed then only that reflected by the fiber surfaces can contribute to the reflectance of the sample and, assuming no changes in the refractive index of the fiber, that ratio has to be one also. At all intermediate absorption conditions, that ratio could have values larger or smaller than one. Experimental evidence and the calculations of Allen and Goldfinger and also of Garrett and Peters (4) show that this ratio is larger than one.

Since the treatment of Kubelka and Munk does not provide for any reflectance at the air-fiber interface, one cannot expect any valid predictions at low reflectances, i.e., at high K/S values. However, as shown in Figure 4, Kubelka-Munk computations based even on high reflectance data give entirely erroneous predictions even for the reflectance ranges for which that approach is supposed to be valid. By contrast, the predictions based on the calculations of Allen and Goldfinger are supported by the experimental results.

The authors are grateful to E. I. du Pont de Nemours & Co., Inc., for the nylon filament and to the GAF Corporation for the Dye. This paper contains some of the results K. C. Lau will submit as his thesis in partial fulfillment of the requirements for the degree of Master of Science in Textile Chemistry.

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Received May 22, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 485–486 (1973)

GRAPHICAL SOLUTION OF THE MARTIN EQUATION

The Martin equation has been widely used for correlating the viscosity of polymer solutions because it can cover such a wide range of concentrations (1, 2). The equation is

$$\log [(\eta_r - 1)/c] = \log [\eta] + K [\eta] c \tag{1}$$

where η_r is the relative viscosity, the ratio of solution viscosity to solvent viscosity; c is concentration (g/dl), $[\eta]$ is intrinsic viscosity (dl/g); and K is a constant for a given polymer-solvent combination. Representative values of K have been tabulated (1).

Once K has been established for a polymer-solvent system, $[\eta]$ can be determined from a single set of η_r, c. However, because of the form of the Martin equation $[\eta]$ (or $[\eta]c$) must be obtained by successive approximations. A graphical approach obviates the trial-and-error solution. Equation (1) can be expressed by a determinant:

$$\begin{vmatrix} \log [F_2 (\eta_r - 1)] & 1 & 1 \\ -F_1 K & 0 & 1 \\ \dfrac{F_1 \log (F_2 [\eta] c)}{F_1 + [\eta] c} & \dfrac{F_1}{F_1 + [\eta] c} & 1 \end{vmatrix} = 0 \tag{2}$$

where F_1 and F_2 are constants for adjusting scales. They drop out when the determinant is expanded. A nomograph can be constructed based on the determinant in this form (3). The first two columns of each row give the coordinates for an axis for the variable in that row. The product $[\eta]c$ is treated as a single variable here for convenience.

In Figure 1, $F_1 = 2$ is used to expand the K scale with respect to the others. The factor $\log F_2$ is chosen to shift the $(\eta_r - 1)$ scale by one decade at a time. The result is a unique solution for $[\eta]c$ from each set of K, $(\eta_r - 1)$.

For example, if $K = 0.20$ and $(\eta_r - 1) = 40$ (or 4.0×10^1), the line connecting the top and bottom scales intersects the line for a = 1 at $[\eta]c = 4.7$. If a more precise value of $[\eta]c$ is desired, the approximate value from the graph can be used to get an explicit solution. Let x be the value of $[\eta]c$ from the graph and define y by

$$\log y = \log (\eta_r - 1) - Kx \tag{3}$$

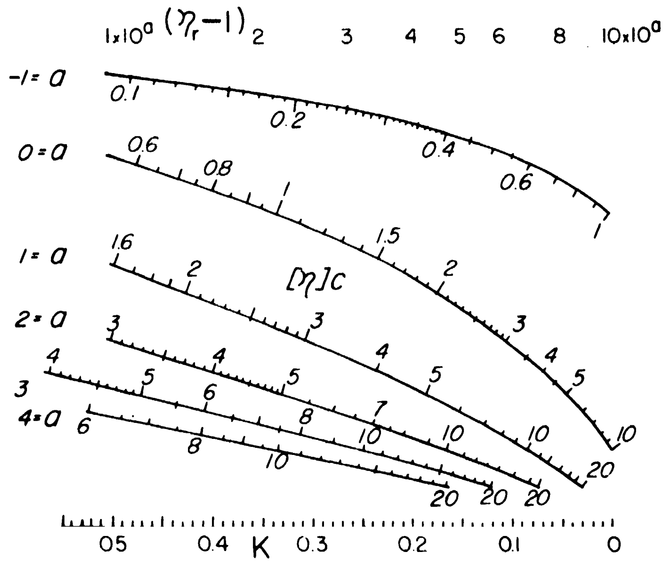

Fig. 1. Nomograph based on Martin Equation.

Then, to a good approximation,

$$([\eta]c)/x - 1 = (y - x)/[x(1 + 2.303\ Kx)] \qquad (4)$$

For the previous example, where $x = 4.7$, eq. (3) gives $y = 4.5926$, and eq. (4) gives $[\eta]c = 4.666$.

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Received June 6, 1973
Revised June 28, 1973

BOOK REVIEWS

Anelastic Relaxation in Crystalline Solids, A. S. Nowick and B. S. Berry, Academic Press, New York and London, 1972. 677 pp. $22.50

Polymer scientists tend to think of viscoelasticity as a phenomenon of special interest in their own field; many are unaware of its importance in metals, salts, gases, and liquids. Indeed, many of the developments in viscoelasticity and much of the impetus for studying it in recent decades have come from those interested in polymers. This fact is made clear in this volume on crystalline solids by the fact that almost all the references in the first four chapters, which deal with the basic phenomeological theory, are to the polymer literature (e.g. Leaderman, Ferry, Tobolsky, Gross, Schwarzl and Staverman, McCrum, Read and Williams).

The authors planned this book as "a textbook and up-to-date monograph on anelasticity in crystals" which deals with "the enormous growth in the literature of the subject [that] has taken place" in the years since C. Zener published his pioneering monograph "Elasticity and Anelasticity of Metals" in 1948. The subject attracted this interest when it "became apparent that the study of anelastic relaxation could contribute greatly to our understanding of almost the whole gamut of physical and chemical phenomena in crystalline solids".

[To the polymer scientist there is a bit of nomenclature problem. What this book calls anelasticity refers to the behavior which he associates with the term viscoelastic solid. What the book calls a linear viscoelastic solid (page 6f.), he would name a linear viscoelastic fluid since in creep, the strain asymptotically approaches linearity with time and there is incomplete recovery. But the experienced rheologist knows that he has to be on guard against inconsistent use of nomenclature even among authors working only on polymers.]

The first six chapters deal with the phenomenological theory of viscoelasticity. Chapter 7 which gives a background discussion of point defects is followed by four chapters dealing with relaxations attributed to this cause. Following Chapter 12, "Dislocations and Crystal Boundaries", two chapters deal with relaxations assigned to dislocations, and one to boundary relaxations. Then come separate chapters on relaxations arising from phase transitions, thermoelasticity, and interaction of acoustic waves with lattice vibrations, magnetic effects, and interactions with electrons. The final chapter deals with experimental methods. The five brief appendices, for the most part, are used to elucidate points in the text.

The authors note in the preface that the first six chapters are "equally suitable as an introduction to anelasticity in the noncrystalline state". Indeed,

they have prepared a succinct summary of some of the basic concepts of linear viscoelasticity which should be useful for properly prepared polymer scientists wishing to learn about this field. However, there is, as should be expected, an emphasis on low loss behavior; the reader will, for example, not learn much about the glass to rubber transition here.

A feature that this book has in common with much of the literature on the subject (including that dealing with polymers) is the lack of documentation that the data really represent anelastic behavior, so carefully described in the opening chapters. Almost all the graphs are the type that show plots of loss and modulus at a fixed frequency as a function of temperature; there are relatively few that show actual anelastic behavior, for example, moduli and loss as functions of frequency. There are only a few cases (e.g., p. 491) where the applicability of laws of anelasticity have been verified. Even when a creep and recovery curve is shown (p. 457), there is no indication in the text whether the authors feel that the relation so carefully derived on page 31 is obeyed by the data. Nor do the authors assist us in understanding how viscoelastic properties, introduced as properties of a material, can vary with the dimensions of the sample as discussed in the case of thermal relaxation on page 500. These comments should perhaps not reflect on this particular book but rather on current practice in this field.

To summarize, polymer scientists might find this book useful for its beginning chapters which provide a concise introduction to basic principles of viscoelasticity. On the other hand, the student of polymer rheology will find the rest of the book a convenient summary of the solid state physicist's view of viscoelasticity and may well find ideas that are applicable to appropriate polymeric materials.

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ANNOUNCEMENTS

Recent Advances in Polymer Science
(The Princeton University Conference)

The Princeton University Conference, September 17-18, 1973, a program for the exchange of ideas, is designed to provide wider opportunities for members of the Princeton Faculty to meet with representatives of member organizations and others to consider questions in areas of mutual interest, whatever their source, and to stimulate communication between the interdependent elements of society.

Research in polymer science and engineering has been the foundation on which a whole new industry has developed over the past thirty years. It is the purpose of this conference to bring forward and discuss the latest research results in this field.

Arthur V. Tobolsky was one of the great leaders in this field. In his memory, the program is directed toward the latest developments in areas he pioneered from chemical synthesis to application properties.

The conference directors are Bryce Maxwell and Garth L. Wilkes, both of the Polymer Materials Program, Department of Chemical Engineering, Princeton University.

Additional information can be obtained by contacting The Princeton University Conference, New South Building, Princeton University, New Jersey 08540. Phone 609–452-3372.

Microscopy of Fibers and Polymers

A program in Microscopy of Fibers and Polymers is being offered by the McCrone Research Institute during the period of October 1-5, 1973.

After an introduction to basic crystallography, the physical structure (orientation and crystallinity) of polymers will be discussed. The optical properties determined by crystallographic procedures then permit the identification of polymers and a better understanding of the physical properties (strength in different directions, elongation, clarity, etc.).

For additional information, write to Mrs. Miriam L. Fallert, Registrar, McCrone Research Institute, 2820 South Michigan Avenue, Chicago, Il. 60616. Fee: $325.

The *Journal of Polymer Science* publishes results of fundamental research in all areas of high polymer chemistry and physics. The *Journal* is selective in accepting contributions on the basis of merit and originality. It is not intended as a repository for unevaluated data. Preference is given to contributions that offer new or more comprehensive concepts, interpretations, experimental approaches, and results.

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Three copies of every manuscript are required. They may be submitted to the appropriate editor: C. G. Overberger (chemistry, physical organic chemistry), Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, or T. G Fox (physics, physical chemistry), Mellon Institute, Pittsburgh, Pennsylvania 15213. Alternatively, manuscripts may be submitted through the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201. All other correspondence should be addressed to Periodicals Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016.

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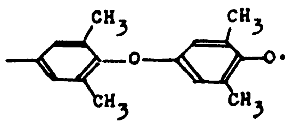
The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition*, monthly; *Polymer Physics Edition*, monthly; *Polymer Letters Edition*, monthly; *Polymer Symposia*, irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition*, *Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

POLYMER LETTERS EDITION VOL. 11, PP. 491–496 (1973)

ELECTRON SPIN RESONANCE STUDIES OF HINDERED ROTATION IN POLY(2,6-DIMETHYL PHENYLENE OXIDE) RADICALS

In previous papers (1,2), we reported an ESR spectrum observed after photolysis at room temperature of benzene solution of poly(2,6-dimethyl phenylene oxide) (PPO). (See Fig. 3 in Reference 1). This spectrum could be attributed to substituted phenoxy radicals of the type (I). The coupling constants



(I)

are $a_{Me}(I) = 5.13$ gauss, $a_{Me}(II) = 6.20$ gauss and $a_H(m) = 1.14$ gauss. It is apparent from these values that two methyl groups are not magnetically equivalent. Although the exact reason for this inequality is not known, this has been interpreted tentatively as a hindered rotation about the bridging O–C bond, and a preferred conformation rendering the radical asymmetric (3). If this interpretation is correct, it is expected that two methyl groups would be equivalent at temperatures high enough to make the rotation free. Therefore, in the present investigation, ESR spectra due to the free radicals (I) were recorded during ultraviolet irradiation at higher temperatures by using variable temperature accessories, and it was found that line width alternation (4) took place at higher temperatures and two methyl groups became equivalent at about 150°C.

The methods of ESR measurement and ultraviolet irradiation have already been described elsewhere (5,6).

Figure 1 shows spectra observed at several temperatures between 60°C and 150°C. The spectrum observed at 60°C has the same number of hyperfine structures as that observed at room temperature, (c.f. Fig. 9 in Reference 2). The intensity ratio, however, is a little different. The spectrum at 88°C showed drastic change in intensity ratio of the hyperfine structure, but four-line substructures were still observed at a central part of the spectrum. At 100°C, however, a central part became an apparent three-line and the intensity of the central part was minimum at this temperature among a series of ESR spectra at various temperatures. The line width alternation was clearly observed in the series of spectra. At temperatures higher than 120°C, the line widths became gradually narrower and at 150°C a sharp seven-line spectrum, each line splitting into three-line substructures, were observed as shown in

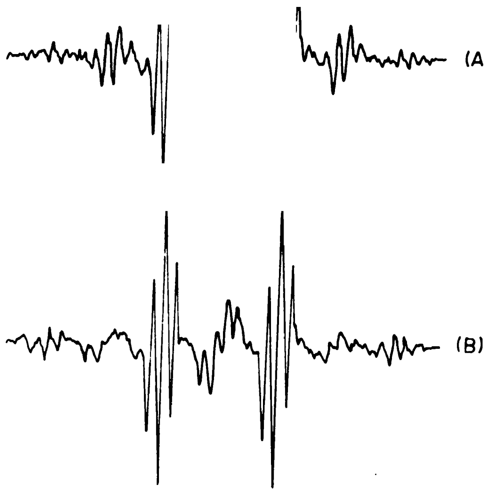


Fig. 1a and b

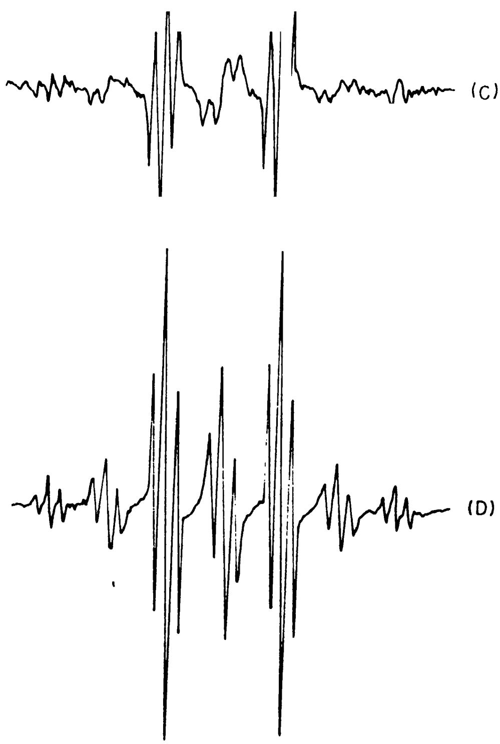


Fig. 1c and d

Fig. 1e

Fig. 1. ESR spectra of xylene solution of poly(2,6-dimethyl phenylene oxide) during irradiation at various temperatures: (A) 60°C, (B) 88°C; (C) 100°C; (D) 120°C; and (E) 150°C.

Figure 1(E). This spectrum can reasonably be attributed to the free radicals (I), which has two magnetically equivalent methyl groups. The obtained coupling constants are a_{Me} = 5.63 gauss and $a_H(m)$ = 1.23 gauss. The observed spectrum was simulated quite well by using these values. This coupling constant for two equivalent methyl groups is very close to an average of two unequal coupling constants obtained at room temperature. This result indicates that the rotation about the O–C bond becomes free at this temperature. Therefore, from these results, the hindered rotation model mentioned above seems to be reasonable.

Hypothetical spectral change with the rate of rotation (or exchange) is shown in Figure 2 by a block diagram, considering the splitting due to only two methyl groups for simplicity. Two meta protons only split each line further into three-line substructures. When rotation frequency is very slow and two methyl groups are not equivalent, a spectrum of Figure 2(A) is expected, while a seven-line spectrum as in Figure 2(C) will be observed at higher rate of rotation. At intermediate rate, a spectrum of Figure 2(B) is observed, where the lines of $M_1 + M_2 = -2$, 0 and 2 become broader. This tendency is consistent with the present observation.

The temperature dependence of the line-widths of $M = \pm 2$ lines was measured at temperatures between 100°C and 150°C. The line widths of the broadened lines were obtained by comparison of the observed signal heights with the theoretical intensity ratios, taking the signal intensity as a product of a square of line width and signal height. An unbroadened intrinsic line width was taken as 0.6 gauss, based on comparison of a simulated spectrum with observed one. ΔH_{msl} (line width at the maximum slope) relates to T_2, spin-spin relaxation time, by the following equation assuming a Lorentzian line shape,

$$T_2 \; \Delta H_{msl} = h(\sqrt{3}\pi \; g\beta)^{-1} \qquad (1)$$

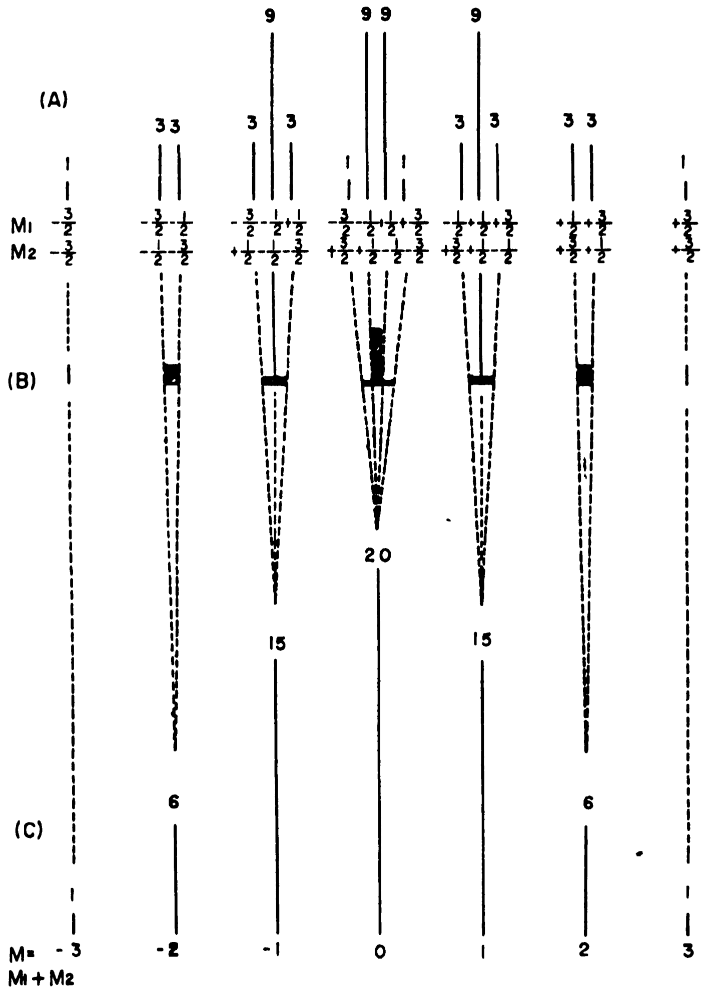


Figure 2. Hypothetical spectra for six equivalent protons comprised of two completely equivalent methyl groups at (A) slow; (B) intermediate, and (C) fast rates of exchanges.

where h is Planck's constant, g is a g value of free electron and β is Bohr magneton. The following relation can also be obtained by solving a modified Bloch equation (7), when rotation is a little fast but the two methyl groups are not completely equivalent.

$$\Delta(1/T_2) = 1/T_2' - 1/T_2 = (\pi^2/2)\, \tau\, (a^A - a^B)^2\, (m_A - m_B)^2 \qquad (2)$$

where $1/\tau$ is a rate of rotation, a^A and a^B are two coupling constants in fre-

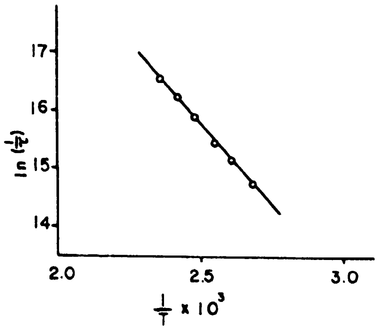


Fig. 3. Arrhenius Plot of $1/\tau$.

quency of unequivalent methyl groups (5.13 and 6.20 X (2.802 X 10^6) cycle), and m_A and m_B are spin quantum numbers of two methyl groups. $\Delta(1/T_2)$ is an increase of $1/T_2$ from the value of $1/T_2$ at no broadening. When M = ± 2 lines are considered, $(m_A - m_B)^2 = 1$ and $(a^A - a^B)^2 = (6.20 - 5.13)^2 \times (2.802)^2 \times 10^{12}$. Therefore τ was calculated according to equation (2) for M = ± 2 lines at several temperatures between 100°C and 150°C, and a value of an order of 10^{-7} sec was obtained. An Arrhenius plot of $1/\tau$ (8) is shown in Figure 3. The activation energy of about 11 kcal/mol was obtained from the slope. This value seems to be consistent with the value obtained from mechanical relaxation measurement (9).

The authors are indebted to the company for permission to publish these results. Thanks are also due to Dr. Iwasaki of Government Industrial Research Institute in Nagoya, and Dr. Shiga of Kyoto University for their kindness to simulate the spectra.

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Received April 24, 1973
Revised June 11, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 497–501 (1973)

CATIONIC POLYMERIZATION OF CYCLIC IMINES. II. 300 MHz ^{1}H-NMR STUDY OF THE STRUCTURE AND CONCENTRATION OF PROPAGATING SPECIES DURING THE POLYMERIZATION OF 1,3,3-TRIMETHYLAZETIDINE.

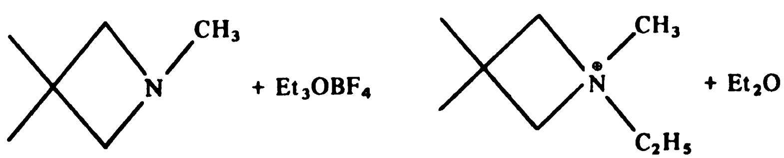
One of the major difficulties in determining the rate constants of propagation and of termination of a polymerization reaction, is to know the concentration of the propagating species during the polymerization. Up to now, in cationic polymerizations this problem has been approached by conductivity measurements (1–3) or by chemical methods (4,5).

Recently we reported that it was possible to determine the concentration of the growing species during the polymerization of 3,3-dimethylthietane (6) by 300 MHz NMR spectroscopy. The great advantage of this method is that the growing chains (cyclic onium salts) can be distinguished from terminated polymer chains (linear onium salts). This is not possible with the previous methods.

In this letter we wish to report the determination of the concentration and structure of the growing species during cationic polymerization of 1,3,3-trimethylazetidine (TMA, I) under the influence of triethyloxonium tetrafluoroborate (TEFB) in nitrobenzene. The kinetics of this polymerization and the polymerization mechanism derived therefrom have been published recently (7).

At room temperature, the reaction between TMA and TEFB produces 1-ethyl-1,3,3-trimethylazetidinium tetrafluoroborate (II, mp 238°C). In this study, II was used as initiator because that way no ether is formed during the initiation reaction. The chemical shift of the methylene protons of diethyl ether is at δ = 3.84 ppm which is the same region as the chemical shift of methylene protons next to an immonium salt function.

Polymerizations were carried out in nitrobenzene at 78°C. In order to evaluate the changes in concentration of the growing chains, a known amount of phenyl benzyl ether was added as an internal standard. Figure 1 shows the δ 3-5 region of the 300 MHz ^{1}H-NMR spectrum of II.



II $BF_4^{\ominus}$

It contains an AB pattern (δ (A) : 4.50 ppm; δ (B) : 4.41 ppm; J(AB) ; 11.4 Hz) due to the nonequivalent methylene protons on the α-carbon atoms of the

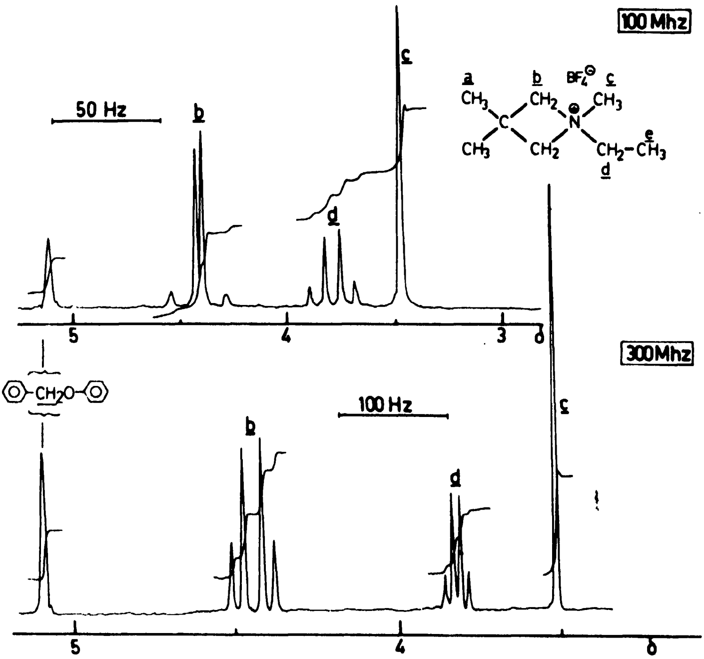


Fig. 1. Detail of the 100 and 300 MHz ^{1}H-NMR spectrum of 1-ethyl-1,3,3-trimethylazetidinium tetrafluoroborate (II) in nitrobenzene at 78°C. Concn.: 0.036 mole-liter^{-1}. Internal standard: benzyl phenyl ether, concn.: 0.026 mole-liter^{-1}.

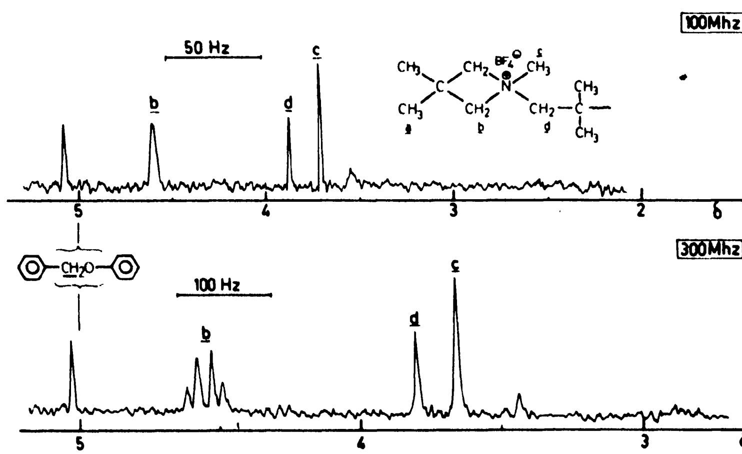


Fig. 2. Detail of the 100 and 300 MHz ^{1}H-NMR spectrum of the reaction mixture of TMA (initial concn.: 0.76 mole-liter^{-1}) with II (initial concn.: 0.036 mole-liter^{-1}) after 10 days at 78°C in nitrobenzene. Internal standard: benzyl phenyl ether, concn. : 0.026 mole-liter^{-1}.

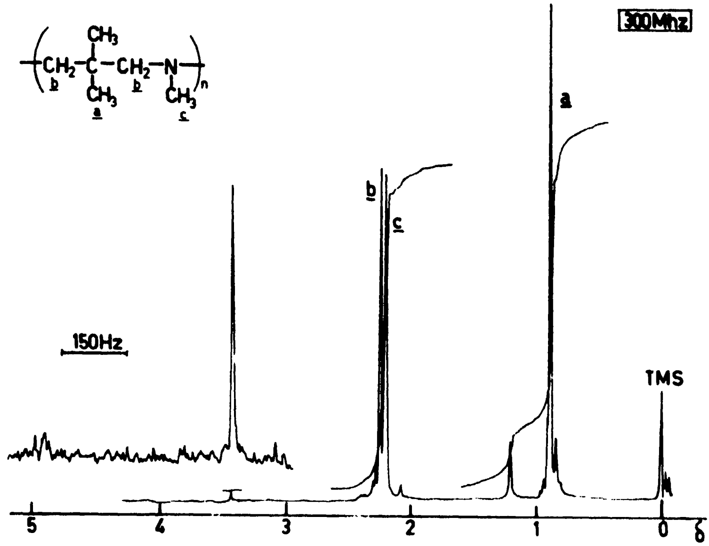


Fig. 3. 300 MHz ^{1}H-NMR spectrum of isolated poly-TMA in deuterated chloroform at 18°C. Concn.: 90 mg/ml.

four-membered ring, a quadruplet (δ : 3.83 ppm) due to the methylene protons of the ethyl group and a singlet (δ : 3.53 ppm) due to the N-methyl protons.

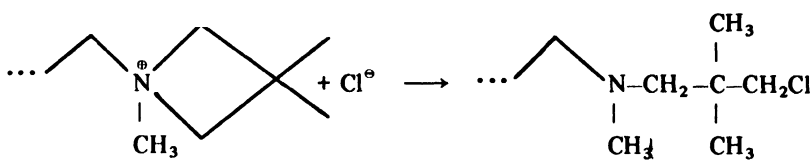
On addition of monomer, the above-mentioned spectrum disappears and instead the following peaks appear : a new AB system (δ(A) : 4.67 ppm; δ(B) : 4.55 ppm; J(AB) : 12 Hz), a singlet at δ: 3.88 ppm and another singlet at δ 3.74 ppm. This is the spectrum of the propagating species which clearly is in accordance with a four-membered ring structure. Its concentration remains constant throughout the whole polymerization time and is equal to the concentration of initiator as is proved by the constant ratio of integrations of growing chain peaks to the internal standard peak. Figure 2 shows the NMR spectrum of the reaction mixture after 10 days at 78°C (100% conversion).

In the figures the 100 MHz spectra of the same reaction mixtures are also shown. The chemical shifts of the methylene protons in the azetidinium ring are nonequivalent, but they have very similar chemical shifts. For the growing chain this nonequivalence is barely evident in the 100 MHz spectrum but the 300 MHz spectrum clearly shows the expected AB pattern. Also, the determination of the concentration is less accurate with the 100 MHz than with the 300 MHz.

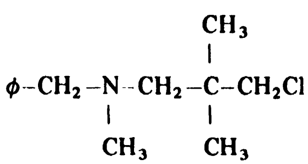
This study confirms the conclusions deduced from the kinetics of similar polymerization reported in a previous paper (7): 1) initiation is very fast compared to the propagation reaction; 2) the concentration of growing chains is equal to the initiator concentration; 3) the growing species are quaternary azetidinium salts; 4) the concentration of growing species remains constant

throughout the whole reaction which means that the polymerization is of the "living" type.

To isolate poly-TMA, the nitrobenzene solution was extracted with 2N aqueous hydrogen chloride, the aqueous layer was treated with sodium hydroxide and the resulting emulsion was extracted with methylene chloride. Figure 3 shows the entire NMR spectrum of poly-TMA isolated that way. As shown by the inserted amplified spectrum, the growing chains have disappeared. The singlet at δ 3.45 ppm could be attributed to the presence of an alkyl chloride function formed by nucleophilic attack of a chloride ion on the azetidinium ion during the extraction of polymer with hydrogen chloride.



The observed value of δ 3.45 is very close to the chemical shift of similar methylene protons in substance III (δ = 3.47 ppm) which has an analogous structure and which is obtained from TMA and benzyl chloride (7).



III

The singlet at δ 1.21 ppm could not be explained.

Financial support received from the Ministry of Science is gratefully acknowledged. E. H. Schacht thanks the "Nationaal Fonds voor Wetenschappelijk Onderzoek" for a fellowship.

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Received March 5, 1973
Revised June 26, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 503–513 (1973)

EMULSION POLYMERIZATION: INITIATION OF POLYMERIZATION IN MONOMER DROPLETS

Introduction

It has long been accepted that the principle locus for initiation of emulsion polymerization is the aqueous phase. Two mechanisms have been proposed: 1. Radicals generated in the aqueous phase enter monomer-swollen emulsifier micelles and rapidly polymerize the solubilized monomer, forming a monomer-swollen polymer particle (1,2); 2. Radicals generated in the aqueous phase add solute monomer molecules to form an oligomeric radical which precipitates from solution at a critical chain length to form a stable primary latex particle or to coagulate with a previously-formed polymer particle (3-5). In both mechanisms, the formation of the first polymer molecule results in the formation of a polymer particle, which absorbs monomer and serves as the locus for further polymerization, and the monomer emulsion droplets serve as reservoirs, which feed monomer to the polymerizing particles by diffusion through the aqueous phase. The monomer emulsion droplets are not considered to be significant loci for initiation of polymerization because their overall surface area is relatively small compared to that of the monomer-swollen micelles or primary latex particles, even though initially the bulk of the monomer is in the form of emulsion droplets, with only a small part dissolved in the aqueous phase and solubilized in the micelles.

The basis for the monomer droplet-reservoir hypothesis is the classical work of Stearns (6), who found that the isoprene emulsion droplet phase separated at different conversions by centrifugation contained less than 1% polyisoprene and that 0.5-mm isoprene drops suspended in a polymerizing medium preserved their spherical shape while their volumes decreased about 100-fold, after which their surfaces became distorted because of the now-appreciable polyisoprene content. Harkins (1,2) pointed out that the emulsification of monomer in water usually produces average droplet sizes in the range 2-5 μ and that droplets of this size cannot compete effectively with the much smaller and much more numerous monomer-swollen micelles in capturing radicals formed in the aqueous phase. A similar argument can be made for the mechanism in which the oligomeric radicals formed in the aqueous phase precipitate to form primary latex particles or coagulate with previously-formed particles. If the monomer droplets cannot compete with the micelles or primary latex particles because of their relatively small surface area, the dispersion of the monomer to a much smaller average droplet size, resulting in a drastically-increased surface area, should enhance their importance as loci for initiation of polymerization.

The purpose of this paper is to show how such a sufficiently-small droplet size can be achieved in the emulsion polymerization of styrene by the use of an anionic emulsifier-fatty alcohol combination as emulsifier.

Hypothetical Calculations

That sufficiently-small monomer emulsion droplets can compete effectively with monomer-swollen micelles is shown by the following calculations for a hypothetical 25:75 styrene-water system emulsified with 0.3% sodium lauryl sulfate based on water. The critical micelle concentration of this emulsifier is about 8×10^{-3}M (7-9) and its molecular area about 50 Å^2 (7,8,10). Table I gives values of the numbers of droplets and micelles, as well as the distribution of emulsifier molecules, calculated according to the following assumptions: 1. The surface of the emulsion droplets is saturated with adsorbed emulsifier; 2. The only emulsifier available for the formation of micelles is that remaining in excess of the critical micelle concentration (8×10^{-3}M or 0.22% based on water) after the droplet surface is saturated; 3. Each micelle is comprised of 100 emulsifier molecules and has a diameter of 100 Å; 4. The amount of monomer dissolved in the aqueous phase and solubilized in the micelles can be neglected. It can be seen that the emulsifier concentration in the aqueous phase is insufficient to form micelles at droplet sizes smaller than 2.7 μ. Moreover, at droplet sizes smaller than 0.7 μ, there is no emulsifier in the aqueous phase at all and the total amount present is insufficient to saturate the droplet surfaces (0.3% emulsifier amounts to 6.27×10^{18} molecules/cc H_2O). Usually, the emulsification of styrene in water using oil-in-water emulsifiers produces average droplet sizes in the range 2-5 μ, and only the most vigorous mechanical agitation or homogenization produces average droplet sizes as small as about 1 μ. If it is assumed that radicals generated in the aqueous phase migrate to the monomer-water interface independent of whether that interface is that of a micelle or droplet, radical entry into micelles is favored over that into droplets only for the largest of the emulsion droplet sizes usually produced by emulsification (the probabilities are 85% and 46% for droplet diameters of 5.0 μ and 3.0 μ, respectively). In this case, the micelles are the principal locus for initiation of polymerization, although the contribution of the droplets is not negligible. If the droplet size could be reduced to much smaller values, however, the participation of the droplets as loci for initiation of polymerization would be enhanced greatly, e.g., for droplet sizes of 0.7 μ or smaller, the principal locus for initiation of polymerization should be the droplets.

Table II gives the corresponding values for the second-type system in which the initiation of polymerization occurs by the formation of oligomeric radicals in the aqueous phase. In this case, the hypothetical 25:75 styrene-water system is emulsified with 0.2% sodium lauryl sulfate, a concentration below the critical micelle concentration. The values of the oil-water interfacial areas were calculated using analogous assumptions: 1. The surface of the emulsion droplets is saturated with adsorbed emulsifier; 2. The only emulsifier available to stabilize the primary latex particles is that remaining in excess after the droplet surface is saturated; 3. Each primary latex particle is comprised of a single polystyrene molecule of molecular weight 5×10^5 swollen with an equal weight of styrene monomer, to give an overall particle diameter of 150 Å; 4.

TABLE I

Calculated Number of Micelles and Distribution of Emulsifie

Diameter of styrene emulsion droplets, μ	Number of droplets/cc H_2O	Number of emulsifier molecules/cc H_2O			Number of micelles/cc H_2O
		Droplets, $\times 10^{-18}$	Aqueous phase, $\times 10^{-18}$	Micelles, $\times 10^{-17}$	
5.0	5.63×10^{9}	0.884	5.39	7.89	7.89×10^{15}
3.0	2.61×10^{10}	1.47	4.80	2.00	2.00×10^{15}
2.0	8.79×10^{10}	2.21	4.06	0	0
1.0	7.03×10^{11}	4.42	1.85	0	0
0.7	2.05×10^{12}	6.27	0	0	0

TABLE II

Calculated Number of Primary Latex Particles and Distribution of Emulsifier

Diameter of styrene emulsion droplets, μ	Number of droplets/cc H_2O	Number of emulsifier molecules/cc H_2O		Number of primary particles/cc H_2O
		Droplets, $\times 10^{-18}$	Primary particles, $\times 10^{-18}$	
5.0	5.63×10^{9}	0.884	3.30	2.33×10^{15}
3.0	2.61×10^{10}	1.47	2.71	1.92×10^{15}
2.0	8.79×10^{10}	2.21	1.97	1.40×10^{15}
1.1	5.29×10^{11}	4.18	0	0

The surface of each primary particle is saturated with adsorbed emulsifier; 5. The number of primary particles is determined by the amount of emulsifier available to saturate their surface; and 6. The amount of monomer dissolved in the aqueous phase or the primary particles, as well as the amount of polymer comprising the primary particles, can be neglected. It can be seen that at droplet sizes of 1.1 μ and smaller all of the emulsifier is on the surface of the droplets and none is available to stabilize the primary latex particles (0.2% emulsifier amounts to 4.18×10^{18} molecules/cc H_2O). Thus, as with the first-type system, a radical generated in the aqueous phase is more likely to enter a primary latex particle than a monomer droplet only for the largest of the emulsion droplet sizes (the probabilities are 79%, 65%, and 47% for droplet diameters of 5.0 μ, 3.0 μ, and 2.0 μ, respectively). At droplet sizes of 1.1 μ or smaller, however, the principal locus of the initiation of polymerization should be the droplets.

Earlier Work

It has long been known that the addition of long-chain fatty alcohols drastically increases the capacity of anionic emulsifiers to disperse and stabilize oil-in-water emulsions (11). Recently, Ugelstad et al. (12) described the use of anionic emulsifier-fatty alcohol combinations in the emulsion polymerization of vinyl chloride and suggested (13) that the effect of certain fatty alcohols on the kinetics of the reaction and the particle size produced might be explained by initiation of polymerization in the monomer droplets. This suggestion was supported by the observation that the addition of long-chain fatty alcohols lead to a marked increase in the stability of the monomer emulsion, which in turn is ascribed to the formation of monomer droplets of smaller size. Also, Vanderhoff et al. (14) presented evidence for the initiation of polymerization in emulsion droplets in the inverse emulsion polymerization of 20% aqueous p-sodium styrene sulfonate in a continuous xylene phase using Span 60 as emulsifier and benzoyl peroxide as initiator. However, the evidence for initiation of polymerization in vinyl chloride emulsion droplets is mostly indirect, i.e., based on conversion-time curves and final latex particle sizes, and it was not possible to determine the droplet size of the vinyl chloride emulsion directly. Initiation of polymerization in aqueous p-sodium styrene sulfonate droplets as small as 300 Å in diameter was demonstrated by the electron microscopic examination of aqueous poly-p-sodium styrene sulfonate solutions dispersed in xylene using the same conditions as with the monomers; however, this polymerization system is unusual in that the interfacial tension between the xylene and monomer phases is, perhaps fortuitously, essentially zero and, hence, an extremely-small droplet size is to be expected.

Experimental Details

Emulsion polymerization experiments were carried out using styrene as mon-

omer, to determine if these earlier results could be applied to a monomer often used as a standard in emulsion polymerization studies. The polymerization recipe used is given in Table III. The styrene (Eastman Kodak Company) was distilled under vacuum to remove the inhibitor and stored at 4°C until used. Laboratory deionized water was used throughout. The sodium lauryl sulfate and cetyl alcohol were Fisher Scientific Company laboratory grade, the potassium persulfate Fisher certified grade.

TABLE III

Polymerization Recipe

Deionized water	75.00 g
Inhibitor-free styrene	25.00 g
Sodium lauryl sulfate	0.10, 0.20, or 0.40 g
Cetyl alcohol	0.40 or 0.80 g
Potassium persulfate	0.25 g

The styrene emulsions were prepared by stirring the aqueous solution of emulsifier and fatty alcohol in a 250-ml Erlenmeyer flask at 300 RPM for ½ hour at 60°C, then adding the styrene monomer under nitrogen and stirring for another ½ hour. At this stage, samples were taken for examination of the stability of the monomer emulsion and for optical microscopy to determine the average droplet size. Emulsions were prepared using three different sodium lauryl sulfate–cetyl alcohol combinations (0.1–0.4, 0.2–0.4, 0.4–0.8 g) and three different concentrations of sodium lauryl sulfate alone (0.1, 0.2, 0.4 g).

The styrene emulsions (still at 60°C) were transferred to 4-oz glass bottles fitted with screw caps containing self-sealing gaskets ("sandwich" of B. F. Goodrich W-7 butyl rubber and W-9 50:50 PVC–SBR mixture). The atmosphere was flushed with nitrogen by inserting two hypodermic needles through the gasket, one connected to the nitrogen supply, and the other providing an outlet. The potassium persulfate solution was then injected through the gasket, and the polymerization was carried out to high conversion under constant shaking at 60°C. The latexes were cooled and examined by both optical microscopy and electron microscopy.

The optical microscopic examination used the dark-field phase-contrast optics, which distinguishes emulsion droplets as small as 0.2 μ in diameter; however, the photographs made with these optics showed less detail than was visible to the eye or seen in photographs made with ordinary optics, which distinguish emulsion droplets as small as 0.5 μ in diameter. Therefore, the observations reported below were made using the dark-field phase-contrast optics, but the photographs were made with the ordinary optics. The electron micro-

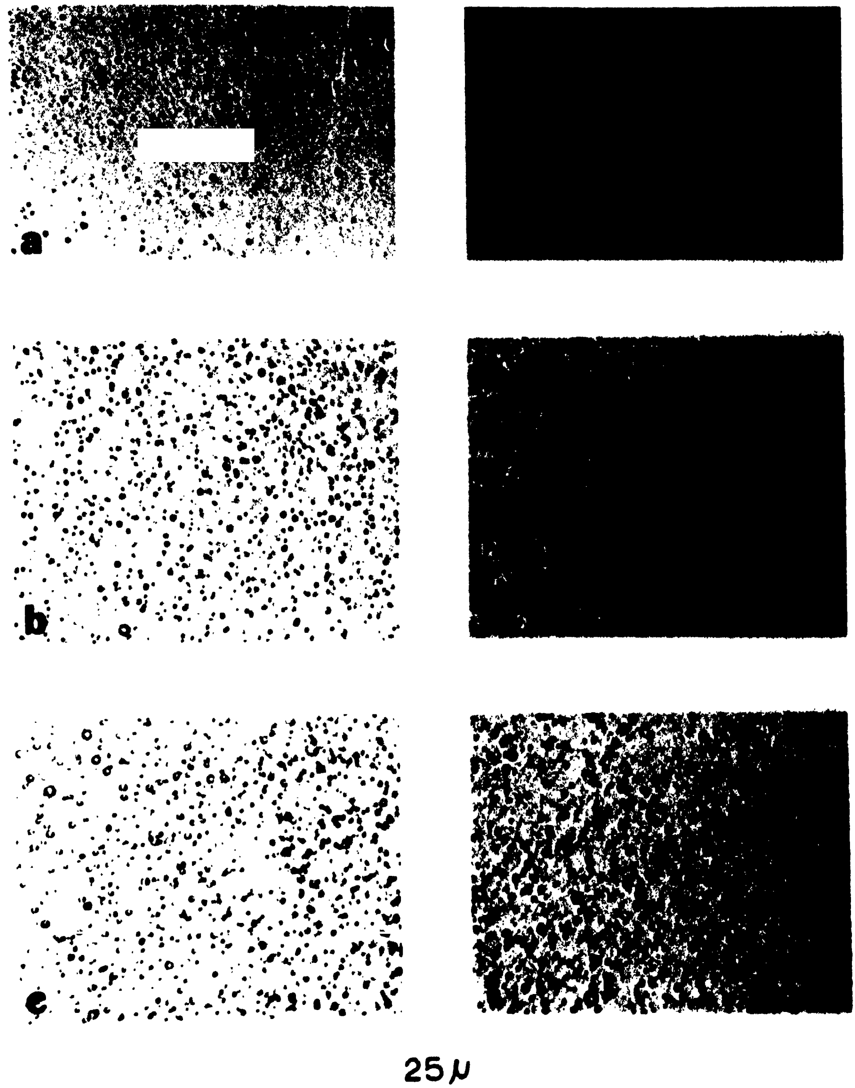

Fig. 1. Optical photomicrographs of styrene emulsions (a–c) and the corresponding polystyrene latexes (d–f) prepared using the following proportions of the sodium lauryl sulfate-cetyl alcohol combination: a, d. 0.4–0.8 g; b, e. 0.2–0.4 g; c, f. 0.1–0.4 g.

graphs were made by drying latexes diluted to about 10 ppm polymer on specimen substrates and examining the specimens in a Phillips Model EM 300 electron microscope.

Results and Discussion

The styrene emulsions made with sodium lauryl sulfate alone were very unstable and separated within a few minutes when the stirring was stopped. The emulsions made with the sodium lauryl sulfate–cetyl alcohol combinations, however, were much more stable and showed no signs of separation after standing for 2 weeks. Thus, the addition of cetyl alcohol to the sodium lauryl sulfate formed a more stable emulsion than with sodium lauryl sulfate alone.

Figure 1 shows optical photomicrographs of the styrene emulsions (Figs. 1a–c) and the corresponding polystyrene latexes (Figs. 1d–f) prepared with the sodium lauryl sulfate–cetyl alcohol combinations. In all styrene emulsions, the bulk of the monomer is in the form of droplets with diameters less than 1 μ. Moreover, an increase in the concentration of the sodium lauryl sulfate–cetyl alcohol combination gives more uniform and smaller-size emulsion droplets, as well as a substantial decrease in the number of the larger-size droplets. Note the striking similarity between the size distributions of the emulsions and the corresponding latexes for the systems prepared using sodium lauryl sulfate–cetyl alcohol combinations 0.1–0.4 (Figs. 1c and 1f) and 0.2–0.4 (Figs. 1b and 1e). This is not the case with the 0.4–0.8 system which showed more microscopic-size droplets in the emulsion (Fig. 1a) than in the latex (Fig. 1d).

Figure 2 shows electron micrographs of the latexes prepared with the sodium lauryl sulfate–cetyl alcohol combination (Figs. 2a–c) and the corresponding amounts of sodium lauryl sulfate alone (Figs. 2d–f). Generally, the average particle diameters of the former series are larger than those of the corresponding samples of the latter series. In both series, the average particle diameter increases with decreasing emulsifier concentration. With sodium lauryl sulfate alone (Figs. 2d–f), the width of the particle-size distribution decreases with decreasing emulsifier concentration. This is contrary to the mixed emulsifier system (Figs. 2a–c) in which the width of the particle size distribution increases with decreasing emulsifier concentration.

The results for the sample prepared with the highest concentration of the sodium lauryl sulfate–cetyl alcohol combination (0.4–0.8) are attributed mainly to initiation in the aqueous phase. The number of microscopic-size particles in the final latex (Fig. 1d) is much smaller than in the original emulsion (Fig. 1a), indicating that many emulsion droplets disappeared during polymerization and thus were not significant loci for polymerization initiation.

More recent experiments (15) showed that an increase in the concentration of the mixed emulsifier system beyond a certain limit results in a marked increase in the proportion of emulsifier which remained in the water phase after emulsification of the monomer (below this limit, practically all of the emulsifier was adsorbed on the monomer droplets). Apparently, an increase in concentration beyond this limit gave only a small further decrease in the size of the monomer droplets and a sufficient concentration of emulsifier in the aqueous phast to initiate a significant number of latex particles. With the highest concentration of the sodium lauryl sulfate–cetyl alcohol combination used here

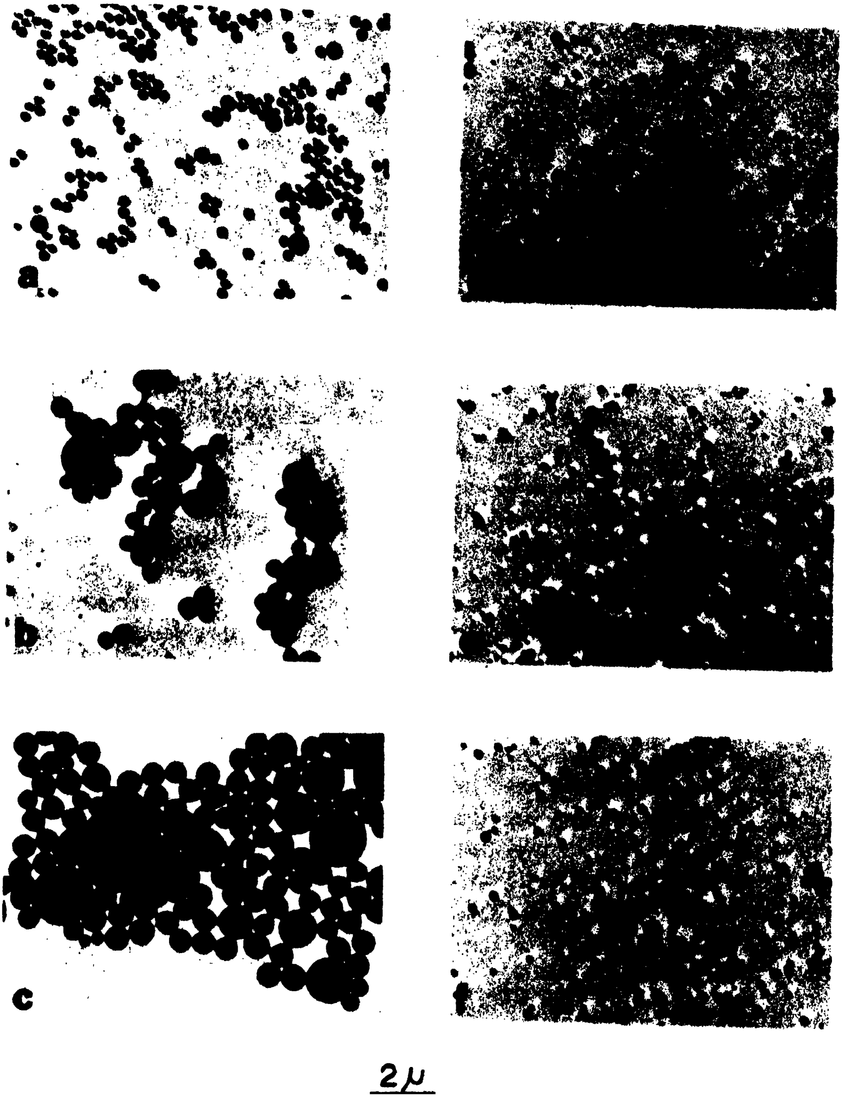

Fig. 2. Electron micrographs of polystyrene latexes prepared with sodium lauryl sulfate–cetyl alcohol combinations (a–c) and sodium lauryl sulfate alone (d–f) in the following proportions: a. 0.4–0.8 g; b. 0.2–0.4 g; c. 0.1–0.4 g; d. 0.4 g; e. 0.2 g; f. 0.1 g.

(0.4–0.8 or 0.53% sodium lauryl sulfate), the larger-size particles of the bimodal particle-size distribution are attributed to initiation in the monomer droplets and the smaller-size particles, to initiation in the aqueous phase (in this latter case, the emulsifier concentration in the aqueous phase was probably less than the 0.13% of sample 2f because the average particle size is larger).

The results for the samples prepared with the lower concentrations of the sodium lauryl sulfate–cetyl alcohol combination, however, are attributed mainly to initiation in the monomer droplet phase. In these cases, the number and size of the microscopic-size particles are the same for both the original emulsions (Figs. 1b and 1c) and the final latexes (Figs. 1e and 1f), the size distributions (Figs. 1e and 1f) are consistent with the electron micrographs (Figs. 2b and 2c), and the width of the particle-size distribution increases with decreasing emulsifier concentration (contrary to conventional emulsifiers with which it decreases with decreasing emulsifier concentration). All these results support our contention that the monomer droplets were a significant loci for polymerization initiation.

Conclusions

There are significant differences in the results obtained with the sodium lauryl sulfate–cetyl alcohol combinations and sodium lauryl sulfate alone. With sodium lauryl sulfate alone, the stability of the styrene emulsion is poor, its average droplet size is large, and the average particle size of the latex produced is very small. With the combination, the stability of the styrene emulsion is very good, its average droplet size is very small, and the average particle size of the latex produced is about the same as that of the monomer emulsion, much larger than with sodium lauryl sulfate alone.

This reduction in average size makes the monomer emulsion droplet more competitive in capturing radicals generated in the aqueous phase because: 1. The surface area of the droplets is increased greatly by the reduction in average size; and 2. The greatly increased amount of emulsifier adsorbed on the droplet surfaces reduces its concentration in the aqueous phase, i.e., available for particle initiation.

Further experiments on the mechanism of emulsification of monomer, the distribution of emulsifier between the monomer droplet surface and the aqueous phase, and the effect of the fatty alcohols on the kinetics of polymerization will be described elsewhere.

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Revised July 10, 1973

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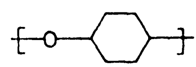
CONFORMATIONAL-INDUCED RELAXATION EFFECTS IN POLYMERS CONTAINING IN-CHAIN ALICYCLIC RING STRUCTURES

Introduction

Molecular motions in polymers containing six-membered alicyclic ring structures have previously been studied for systems in which rings have been positioned pendant to or incorporated in the main chain. Dynamic mechanical properties of systems containing the pendant cyclohexyl group have been intensively studied (1-3). In that work two characteristic transitions have been observed. One occurs at $-3°C$ at 5260 Hz (2) and is attributed to the chair-chair inversion of the rings. This transition is equivalent to $-80°C$ at 1 Hz using the frequency-temperature relationship given by Heijboer (3). The other transition occurs below $-93°C$ at 6380 Hz and is thought to involve motions of the whole cyclohexyl group.

PCHE :



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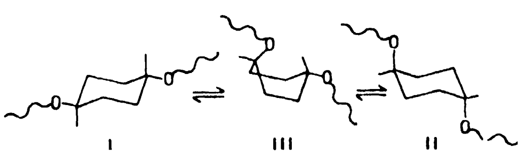

Fig. 1. Conformational forms for the units in poly-(1,4 cyclohexylene ether).

The dynamic mechanical properties of poly-(1,4-cyclohexylene ether), PCHE, derived from 7-oxabicyclo-[2.2.1]-heptane have also been studied (4). This polymer contains cyclohexyl groups incorporated in the chain backbone as shown in Figure 1. A transition has been found at 32°C at 5260 Hz representing an upward shift of some 30°C relative to the peak associated with the chair interconversion in the pendant cyclohexyl group. This shift to a higher temperature is caused by the presence of two bulky substituents, i.e., the polymer chains attached to the 1 and 4 positions. The implication of this is that the ring inversion cannot occur without a conformational reorientation of the main chain. From the high melting point of this polymer it may be assumed that the substituents are trans-positioned (5) and the ground state must be represented by a 1,4-diequatorial chair conformation.

As shown in Figure 1, this conformer may be converted into a 1,4-diaxial

chair conformation or a boat conformation with trans-positioned substituents, and it is not immediately apparent which one of these high energy conformations is the preferred one. In either case a reorientation of chain conformation is required before a ring can undergo inversion. This is a property of 1,4 substituted polyether systems, which is lacking in many cyclohexane-containing polymer systems. Polymers containing other bonds in the main chain capable of undergoing flexing will participate, presumably shifting the transition to lower temperatures (6).

In the present work polymers have been prepared from endo- and exo-2-methyl-7-oxabicyclo-[2.2.1]-heptane (7). These polymers are similar to that shown in Figure 1, but contain a methyl group in the 2 position and are thus referred to as endo- and exo-2-Me-PCHE. These were examined in order to assess the effect of a ring substituent on the cyclohexyl group on the dynamic mechanical behavior of these polymers. Differences in the dynamic mechanical properties can result due to inversion between different conformational forms. In accordance with the mechanism of polymerization of these compounds (7), the chain substituents in the ground states for the polymers of the two isomers are in a 1,4-diequatorial chair conformation and the methyl group is in the equatorial and axial positions for the polymer of the endo- and exo-isomer respectively. This implies that the polymer of the endo-isomer has the lowest energy level in the ground state, since all substituents are equatorially placed. Furthermore, different high energy conformations can result from ring inversions perhaps leading to different mechanical damping transitions for the polymers of the two isomers.

The polymer has also been prepared from endo, exo-2,6 dimethyl-7-oxabicycle-[2.2.1]-heptane. This polymer is also similar to that shown in Figure 1, but is methyl substituted in position 2 and 6, and referred to as endo, exo-2,6 diMe-PCHE. Again, it appears reasonable that the chain substituents in the ground state are in a 1,4 diequatorial chair conformation, and that the methyl groups are axial–equatorial.

Experimental

The dynamic mechanical properties of the above mentioned PCHE derivatives were studied using the method of torsional braid analysis (8). Since only relatively small amounts of the polymers were available and in consideration of the mechanical strength of these polymers, this was the method of choice for performing the dynamic measurements.

This method is very similar to that of the torsional pendulum with the exception that the material to be studied is supported in a glass fiber bundle. The fiber bundles were immersed in 5% solutions of the polymer in m-cresol and subjected to high vacuum (10^{-4} mmHg) to remove the solvent by evaporation. For the dimethyl derivative, a mixture of phenol and sym-tetrachlorethane (100:66 by weight) was used. The logarithmic decrement (Δ), i.e., the damping factor, was determined from the photographic recordings of the damp-

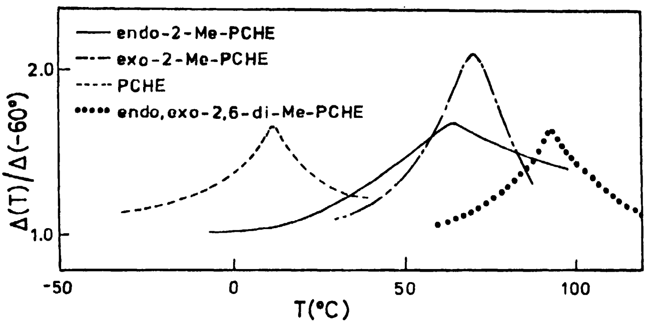

Fig. 2. Smoothed damping curves for the four types of polymers.

ing trace of free oscillations (~ 1 Hz) of an inertial plate suspended by the fiber bundle. Measurements were performed as a function of temperature with a temperature increase at the most of 12°C per hour. As a check on this method, measurements were also performed on PCHE to compare the result with that of previous workers (4).

Result and Discussion

The results obtained on the four PCHE derivatives are shown in Figure 2. The curves have been normalized at −60°C, (Δ(T)/Δ(−60°). This allows a direct comparison, since the normalization procedure cancels out any difference due to variations in the amount of polymer absorbed in the different specimens. The untreated fiberglass shows a damping which is approximately a factor of ten higher than those containing polymer. The important features of these curves are summarized in Table I.

TABLE I

Comparison of the Transitions

Compound	Method	Transition	Ref.
PCHE	Damping factor 5260 Hz	32°C	4
PCHE	Torsional Braid Anal. ~ 1 Hz	12°C	This work
exo-2-Me-PCHE	~ 1 Hz	72°C	This work
endo-2-Me-PCHE	~ 1 Hz	65°C	This work
endo, exo-2,6 di-Me-PCHE	~ 1 Hz	93°C	This work

In comparing the results for PCHE obtained previously and in the present studies, one can see that our result is about 20°C lower than that found previously. This discrepancy can be accounted for by the frequency difference for the two measurements which is almost four decades. The Williams-Landel-Ferry (9) equation predicts a shift of 17°C for four decades of frequency. One can also see that the presence of methyl substituents causes a large increase in the transition temperature; 80°C when going from zero to two methyl groups. This is attributed to increased steric interaction caused by the presence of substituents on the cyclohexyl ring, resulting in decreased chain mobility. Although we feel that the transition involves a chair inversion mechanism an inspection of molecular models plus the observations of previous workers (4) points to chain flexibility as an important factor which may determine whether inversion of the ring can occur.

Comparison of the transitions for the polymers of the endo- and exo-isomer respectively indicates that these are similar in character, implying that the conformational effect is small for the bulk polymers. In light of previous comments, this also is interpreted as arising from similar chain flexibilities. The shape of the transition appears to be dependent on the sample, possibly caused by the method of preparation. The location of the maximum appears, however, to be within ± 5°C.

It should be pointed out, here, that these transitions are relatively weak, less than a factor of 10 in damping between base line and peak maximum, as contrasted to the usual factor of 100 or more (4). This gives a more pronounced scatter in the data and hence our estimate of ± 5°C.

The restricted nature of the cyclohexyl ring inversion for the Me-PCHE isomers has been observed by NMR line broadening techniques (10). One can see, thus, that in complicated ring systems there is a possibility of obtaining conformationally induced relaxation effects. That these effects can be seen in solution, but not in bulk is not particularly surprising. For the polymer in bulk form, it appears that there is a large background resistance to chain motions caused by the highly viscous polymer matrix. This phenomenon of subtle relaxation effects being masked by high activation energies has been discussed in other connections (11,12).

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Received July 12, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 521–523 (1973)

THERMAL DEGRADATION OF ETHYLENE-VINYL ACETATE COPOLYMER

This article presents data from a study of the kinetics of the thermal degradation of ethylene-vinyl acetate copolymer, polymer crosslinking, and electron absorption spectra during degradation.

Ethylene-vinyl acetate copolymer having 38.5 percent by weight of ester groups was used. The copolymer was twice precipitated from toluene into methyl alcohol and dried under vacuum at 50°C over 30 hr. The copolymer was degraded in evacuated (10^{-4} – 10^{-5} mmHg) sealed ampoules with branches at 260-290°C. The products were frozen into branches by liquid nitrogen. Acetic acid was titrated by 0.1N aqueous solution of NaOH. Electron absorption spectra of a 1% toluene solution of the copolymer samples were obtained in the 280-500 nm range by use of a SF-4A spectrometer. The insoluble fraction was determined by filtering the copolymer gel in toluene through a Shotta filter (No. 3).

The main volatile product (>99%) of the thermal degradation of the copolymer is acetic acid. As can be seen from Figure 1, the kinetic curves for thermal deacetylation of the copolymer may be described by the first order reaction equation up to 50-60 percent of conversion. The curves are insignificantly sloped toward the side of decrease of conversion percent. The activation energy, determined from the dependence of log k on 1/T, is equal to 43 ± 1 kcal/mole. The complete expression for rate constant is given by the following Arrhenius equation:

$$k_0 = 7 \times 10^{12} \times e^{-43000/RT} \text{ sec}^{-1}$$

The value of the rate constant k_0 is close to that for thermal degradation of a model low molecular weight compound, secondary butylacetate (1). This fact supports a molecular mechanism of copolymer deacetylation, because it is known (1) that model compounds degrade by a molecular mechanism via the six-membered activated complex.

Copolymer deacetylation proceeds up to 100 percent of conversion with formation of polyethylene macromolecules, containing polyene sequence with a number of conjugated double bonds, nor more than four. This is evidenced by electron absorption spectra of colorless degraded copolymer samples having absorption maximum at 298, 306, and 322 nm.

At the conditions of complete deacetylation of copolymer, that is at 290°C for 300-400 min, polyethylene sequences of macromolecules undergo only insignificant degradation. Mass spectrometric analysis shows that in the volatile products of copolymer degradation, except for acetic acid and the products of its thermal degradation (CH_4 and CO_2), there are small quantities (< 1%) of

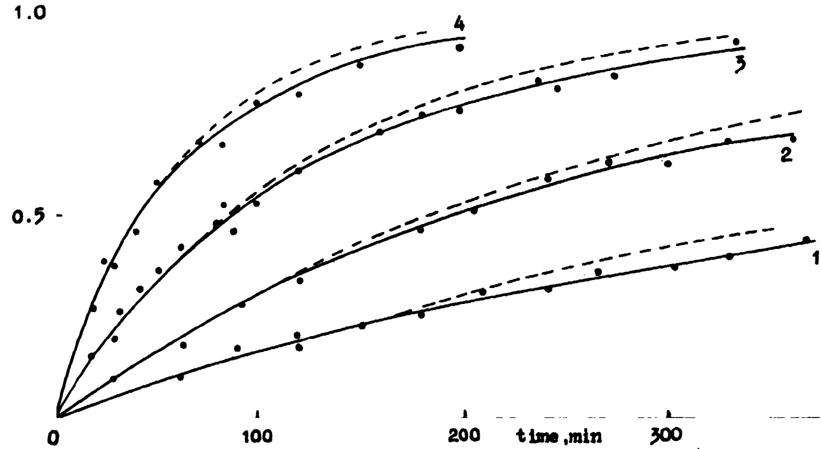

Fig. 1. Deacetylation of ethylene-vinyl acetate copolymer at different temperatures: (1) 260°C; (2) 270°C; (3) 280°C; (4) 290°C.

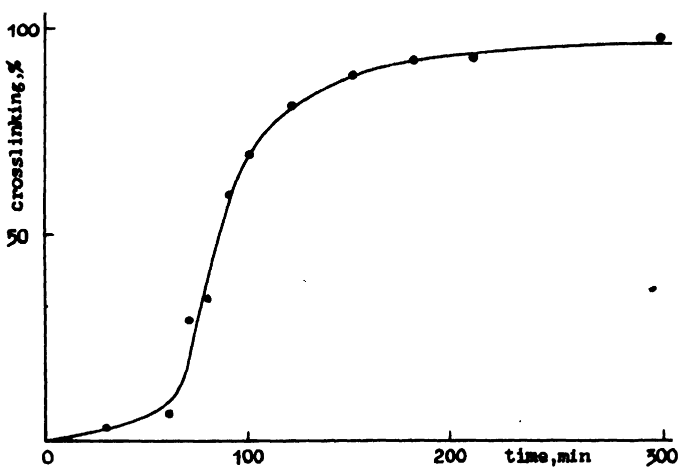

Fig. 2. Dependence of the quantity of insoluble fraction on time for thermal degradation of the copolymer at 260°C.

aliphatic and olefinic hydrocarbons, these being typical products of the thermal degradation of polyethylene (2).

Electron absorption spectra of degraded copolymer also supported the assumption that in the initial product macromolecules are built from alternate links of ethylene (or some ethylene links) and vinyl acetate (2-4 links of vinyl acetate). The probability of discovering macromolecular parts where there are more than four vinyl acetate groups linked with each other is small.

During the thermal degradation, the copolymer crosslinks rapidly. The curve

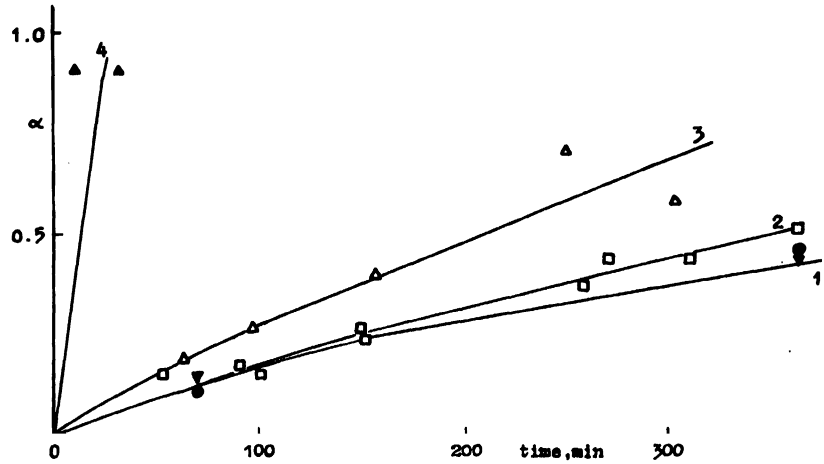

Fig. 3. Deacetylation of copolymer at 260°C: (1) with continuous removal of volatile products by freezing out; (2) without products removal (□) and in the presence of 4.1×10^{-4} mole/g triphenylmethane (▼), 4.4×10^{-4} mole/g 2,4,6-tritert.butylphenol (⊗); (3) 50 mmHg HCl (gas) (△); (4) 5.2×10^{-5} mole/g $SnCl_2$ (▲).

of formation of crosslinked copolymer has an autocatalytic character (Fig. 2). Complete copolymer crosslinking is observed at 40 percent of deacetylation. One can suggest that copolymer crosslinking proceeds by intermolecular cyclization of the polyene sequences of macromolecules.

We have investigated the influence of thermal degradation products and some additives on the process of copolymer deacetylation at 260°C (Fig. 3). Electrophilic reagents (acids, metal chlorides) increase the rate of degradation of vinyl acetate links. Inhibitors of radical reactions do not affect the deacetylation rate. On the basis of these experiments, one can conclude that partially proceeding destruction of polyethylene fragments of macromolecules does not influence the rate of the thermal deacetylation of vinyl acetate links of the copolymer.

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Received June 6, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 525–527 (1973)

THE MOLECULAR ORGANIZATION OF CELLULOSE TRIACETATE MONOLAYERS AT THE AIR-WATER INTERFACE. COMPARISON WITH A MODEL SYSTEM

The properties of cellulose triacetate monolayers spread at the air-water interface have recently been investigated on both a Langmuir (horizontal float) and a Wilhelmy (vertical) film balance (1). Cellulose triacetate formed a condensed, rigid monolayer which introduced problems in the measurement and interpretation of the film properties recorded on the Wilhelmy balance. However with the Langmuir balance it was possible to account for the isotherm characteristics and high surface viscosity in terms of the molecular organization of the monolayer. A mechanism was proposed in which the pyranose rings, initially lying flat on the surface, could tilt laterally during compression to a vertical position with the ring planes perpendicular and the chain axis parallel to the surface. A schematic illustration of this process is shown in Figure 1. It was suggested that the efficient close-packing of chain segments in the tilted state would lead to extensive van der Waals interactions between the hydrophobic surfaces of adjacent glucose residues, producing the high viscosity of the monolayer.

Evidence in support of this mechanism is provided by a recent film balance study of some acetylated disaccharides of glucose spread on 40% ammonium sulfate substrates (2). The monolayer of one of these sugars, cellobiose octa-

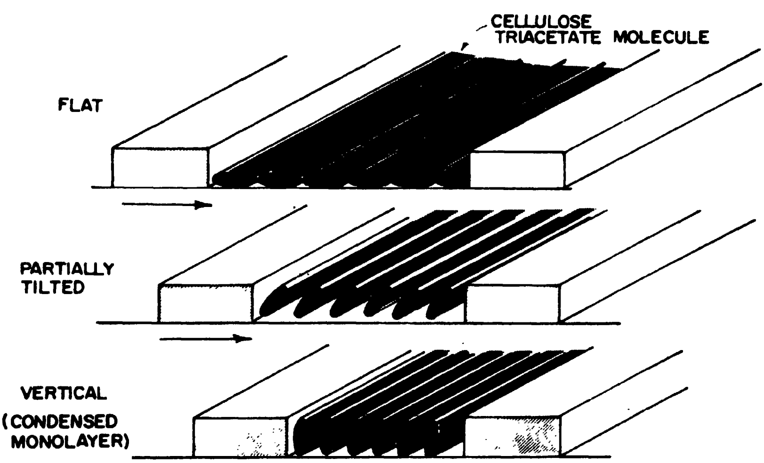

Fig. 1. Schematic representation of molecular tilting during compression of a cellulose triacetate monolayer.

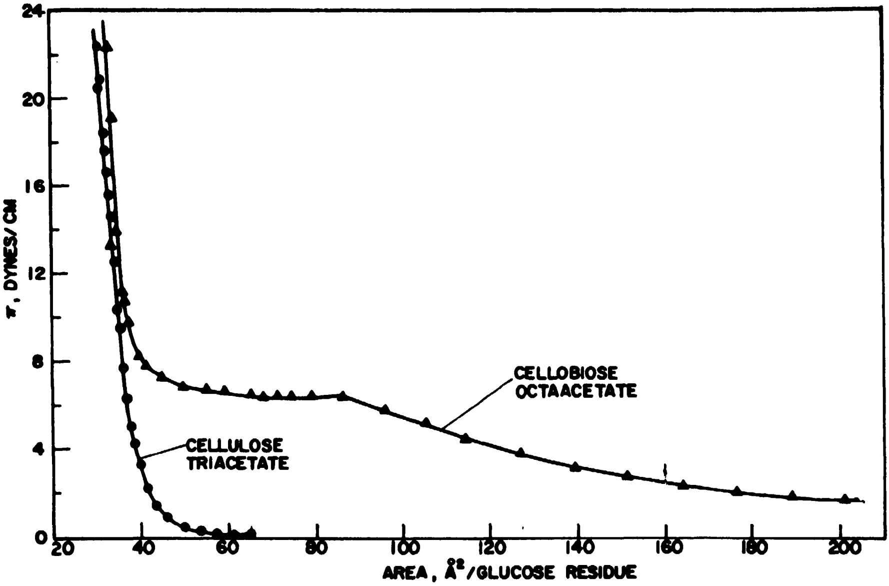

Fig. 2. Pressure-area isotherms for cellulose triacetate and cellobiose octaacetate.

acetate, showed particularly well-defined pressure-area and surface electrical characteristics which could be related unambiguously to a definite molecular rearrangement at the surface. Since this disaccharide can be regarded as a structural model for cellulose triacetate, a comparison of the isotherm characteristics of the two compounds might lead to a more critical assessment of the molecular processes occurring in the monolayer of the parent polysaccharide.

The pressure-area isotherms of cellobiose octaacetate and cellulose triacetate are shown in Figure 2, plotted on the basis of the area per glucose residue. In the sugar isotherm the specific area at the onset of the gaseous-to-solid transition region is consistent with the projected area of a space-filling model in the flat position, while the extrapolated area of the condensed portion (37 Å^2/glucose residue) is compatible with a vertical orientation with the long axis parallel to the surface. The condensed state therefore consists of tightly packed molecules stacked along the surface in a film one glucose residue thick. The calculated film thickness in this state is 12 Å which is in excellent agreement with the height of a vertically tilted molecular model. The analysis indicates that the two glucose residues in the disaccharide molecule behave as a rigid structural unit about the glycosidic linkage, undergoing molecular tilting during compression.

It is apparent from Figure 2 that the solid region of the disaccharide curve is nearly coincident with the cellulose triacetate isotherm (obtained on the Langmuir balance). The similar compressibilities and extrapolated areas of the two isotherms strongly suggest that the glucose residues in the polysaccharide

and disaccharide have the same organization in the condensed state. Consequently, the molecular tilting mechanism originally postulated for the polymer appears to be realistic.

The results imply that cellulose triacetate chains are capable of assuming a high degree of lateral order at the interface. In this regard, it is interesting to note that a monolayer composed of tilted tightly packed cellulosic chains resembles the concept of a cellulose "sheet" introduced by Warwicker et al. to explain swelling reactions of cellulose (3,4). On the basis of x-ray diffraction studies they proposed that flat molecular cellulose ribbons lie on top of each other within the 101 plane, forming a stack (or sheet) one residue thick which acts as the fundamental reacting unit during swelling. Although hydrogen bonding may occur between neighboring chains within the sheet, it appears that the main source of cohesion is nonspecific van der Waals forces between hydrophobic surfaces (3). This further shows the rather close morphological relationship between a cellulose triacetate monolayer and a cellulose sheet.

Contribution No. 79 from the Empire State Paper Research Institute, State University of New York College of Environmental Science and Forestry, Syracuse, New York 13210.

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DEGRADATION MECHANISM OF CROSS-LINKED POLYMERS UNDER DIFFERENT ATMOSPHERE

Recent results on the degradation of cross-linked natural rubber by A. V. Tobolsky et al. (1) suggested main chain scission mechanism for the rubber cured by TMTD (tetramethyl thiuram disulfide) and by dicumyl peroxide in air at high temperature. Their analysis of the effect of cross-linking density on the chemical stress curves measured in vacuo at high temperature (ex. 200°C) indicated that, for the rubber cured by TMTD having carbon–sulfur–carbon cross-links, the cleavage was at the network juncture, and for that cured by dicumyl peroxide having carbon–carbon cross-link the cleavage was along the main chains.

The results shown in Figure 1 were obtained by us for natural rubber cured by sulfur and by TMTD and for EPT (ethylene-propylene terpolymer) cured by sulfur and by TMTD in air at 110°C. In the figure, f(t) is the stress at time t, and f(0) the initially measured stress.

In the figure for EPT cured by TMTD, a straight line was obtained; for EPT cured by sulfur, three straight lines were obtained using Procedure X (2). The slope of the former is equal to that of the uppermost straight line of the latter, an implication of independence of the crosslinking densities n(0). The reasons for these were described in our previous paper (3). For cured natural rubber, a straight line was obtained for that cured by TMTD but not for that

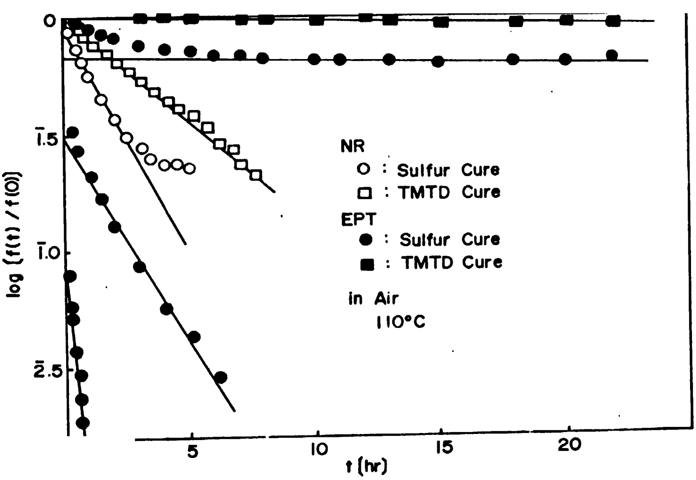

Fig. 1. The relation between log {f(t)/f(0)} vs time for natural rubber vulcanizates with sulfur and TMTD, and EPT vulcanizates with sulfur and TMTD in air at 110°C.

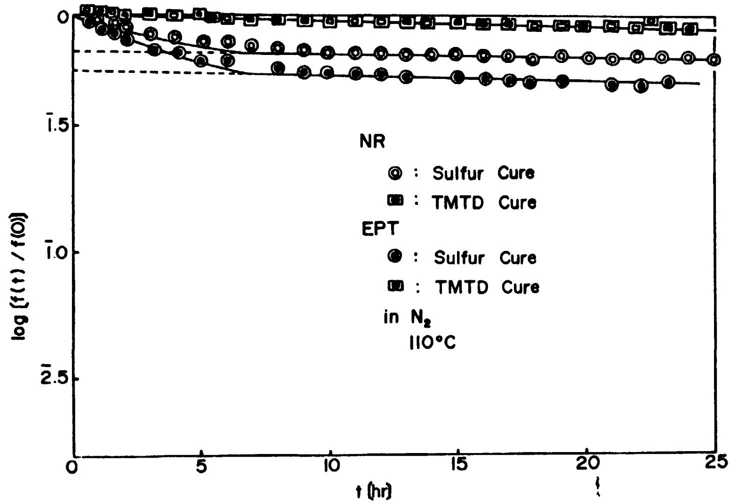

Fig. 2. The relation between log {f(t)/f(0)} vs time for natural rubber vulcanizates with sulfur and TMTD, and EPT vulcanizates with sulfur and TMTD in N_2 at 110°C.

cured by sulfur. The reason is that the chemical stress relaxation curve for rubber vulcanizates cleaving along the main chains can be approximated by a simple Maxwellian decay curve, but for those cured by sulfur having complicated scission mechanism is impossible to express by a simple decay curve.

Experiments in nitrogen atmosphere at 110°C for the above four samples have also been performed, the results were shown in Fig. 2. It was found that both natural rubber and EPT cured by TMTD follow the same straight line, which is also identical to that for EPT cured by TMTD in air at 110°C in Figure 1, indicating an occurrence of scission at cross-links in these samples. The above result for TMTD cured natural rubber in N_2 is consistent with that in vacuo by Tobolsky et al.

In Figure 2, it can also be observed that the slopes of long time side portions of the curves for sulfur cured natural rubber and EPT are identical with those for TMTD cured samples.

From the above results, it is clear that scission at the crosslinks with the exchange reaction of polysulfide linkages occurs in sulfur cured natural rubber and EPT in N_2.

The sulfur-cured natural rubber and EPT in Figure 2 are respectively divided into three straight lines by Procedure X, among which the uppermost one of the three as described above indicates crosslinks scission and the others show exchange scission.

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Received February 14, 1973
Revised July 6, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 533–540 (1973)

ANALYSIS OF CURING KINETICS IN POLYMER COMPOSITES

Abstract

Two analytic methods for evaluating the activation energy, E, the kinetic order, n, and heat of polymerization (or crosslinking), ΔH_p, in polymer matrix composites are developed and applied to differential scanning calorimeter (DSC) data for an epoxy-phenolic adhesive. The first method utilizes a detailed differential-integral analysis of a single DSC curve to isolate E, n, and ΔH_p. The second method utilizes multiple scans at varied scan rate $\phi = dT/dt$ to isolate the ratio E/n. The combined application of these two methods provides an intrinsic test of the basic rate equation and well resolved values of $E = 41.2 \pm 3.6$ kcal/mole, $n = 1.65 \pm 0.23$, and $\Delta H_p = 7.19 \pm 1.03$ cal/g for HT424 adhesive.

Introduction

The isolation of the degree of reaction and kinetics of polymerization of polymer matrix composites remains as one of the important unresolved problems in quality assurance and process control for structural adhesives and fiber reinforced materials. Various methods of thermal analysis, which include dielectric measurement, differential thermal analysis (DTA), and thermomechanical analysis (TMA) have been applied to this problem. (1,2). Of these techniques, one of the least complicated is the direct measurement of the heat of polymerization H_p as determined by differential scanning calorimetry (DSC). This method requires small quantities of material (normally 5 to 15 mg sample) and is rapid (normally 10 to 30 min per scan). The measured value of H_p and its relation to the total heat of polymerization ΔH_p is uncomplicated by complex changes in physical (liquid-solid) state which accompany curing and therefore correlates directly with degree of chemical reaction (2).

In this report two interrelated methods for analyzing the DSC curve are derived from the chemical rate equation for polymerization and crosslinking reactions. These analytic expressions are tested by DSC characterization of a polymer matrix composite comprising on epoxy-phenolic matrix. The differential-integral analysis of the DSC curve utilizes a programmable calculator to permit full evaluation of one scan during the 15 to 30 min period of the second DSC scan.

Theoretical Considerations

Two interrelated methods are developed to determine the activation energy

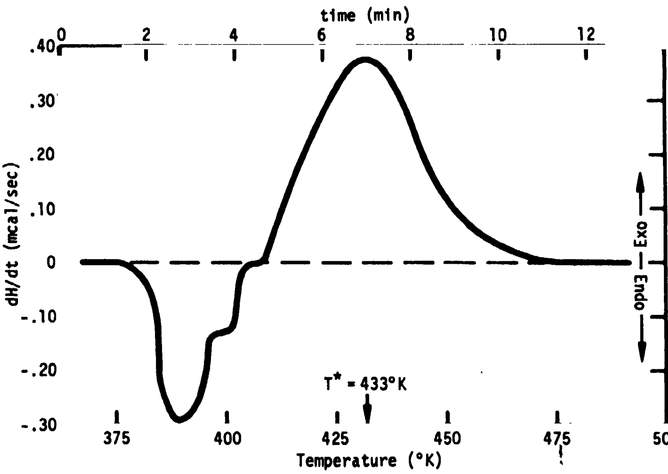

Fig. 1. Typical DSC thermogram of dH/dt versus temperature T for HT424 (ϕ = 10°K/min, Sample No. 3).

E and the kinetic order n for the polymerization (or crosslinking of polymer matrix composites from DSC curves. The first method, suggested by Ellerstein, begins with the assumption that the Arrhenius rate equation applies for the following condensation curing reaction:

$$X + Y \rightleftharpoons C + D\uparrow \tag{1}$$

where X and Y = functional groups, C = a crosslink, and D = a volatile low molecular weight by-product. A general statement for the reaction kinetics is provided by the following relation (3):

$$dx/dt = A(1 - x)^n \exp(-E/RT) \tag{2}$$

where A = frequency factor (assumed constant), n = kinetic order of reaction, E = activation energy, R = gas constant, T = absolute temperature, t = time of reaction, and x = fraction reacted. In a DSC curve of a curing reaction (see Fig. 1) the area beneath the curve equals the total heat of polymerization ΔH_p (2). The partial heat of polymerization H_p varies in direct proportion to the fraction reacted x, thus providing the following relation:

$$x = \frac{H_p}{\Delta H_p} \tag{3}$$

and

$$\frac{dx}{dt} = \frac{1}{\Delta H_p}\left(\frac{dH_p}{dt}\right) \tag{4}$$

Combining eq. 4 with eq. 2 gives:

$$\frac{dH_p}{dt} = A(\Delta H_p)\,(1 - x)^n \exp\,(-\,E/RT) \tag{5}$$

DSC measurements provide a constant thermal scan rate ϕ = dT/dt so that eq. 5 can be rewritten as:

$$\frac{dH_p}{dT} = A\,(\frac{\Delta H_p}{\phi})\,(1 - x)^n \exp\,(-\,E/RT) \tag{6}$$

Differentiating eq. 6 with respect to temperature T gives:

$$\frac{d^2H_p}{dT^2} = A\,(\frac{\Delta H_p}{\phi})\,[(1 - x)^n \frac{E}{RT^2} - n(1 - x)^{n-1} \frac{dx}{dT}]\,\exp(-\,E/RT) \tag{7}$$

Substituting the identity $\frac{(1 - x)^n}{(1 - x)} = (1 - x)^{n-1}$ into eq. 7 followed by factoring $(1 - x)^n$ and substitution of eq. 6 provides the following relation:

$$\frac{d^2H_p}{dT^2} = \frac{dH_p}{dT}\,[\frac{E}{RT^2} - \frac{n}{(1 - x)}\frac{dx}{dT}] \tag{8}$$

Rearrangement of eq. 8 yields:

$$[\frac{(d^2H_p/dT^2)}{dH_p/dT}]\,T^2 = [\frac{E}{R} - \frac{nT^2}{(1 - x)\,\Delta H_p}\,(\frac{dH_p}{dT})] \tag{9}$$

The ordinate of a DSC curve (see Fig. 1) is equal to dH_p/dt, which is converted via the scan rate relation ϕ = dT/dt to become $h = (dH_p/\phi dt) = dH_p/dT$. Hence, the slope S of the curve at temperature T equals $S = d^2H_p/dT^2$. Furthermore, the area r beneath the DSC curve which defines the unreacted functional groups is just $r = (\Delta H_p - H_p) = (1 - x)\,\Delta H_p$. Making the appropriate substitutions in eq. 9, we obtain the final working relation:

$$T^2\,(S/h) = (E/R) - nT^2\,(h/r) \tag{10}$$

Evaluating a DSC curve at varied temperature T for values of h, S, and r, followed by plotting $T^2(S/h)$ as the ordinate versus $T^2(h/r)$ as the abscissa, provides a linear function whose slope defines the kinetic order as $-n$ and whose intercept, at $T^2(h/r) = 0$, defines the activation energy in terms of $E = RT^2$ (S/h).

The second method, derived at the Science Center, starts off with the same

rate law assumptions stated by eq. 1 through eq. 8. Inspection of eq. 8 shows that at a characteristic temperature $T = T^*$ the value of $h = dH_p/dT$ maximizes (see Fig. 1) to provide zero slope $S^* = d^2H_p/(dT^*)^2 = 0$ and the resulting special relation:

$$\frac{dx^*}{dT^*} = \frac{(1 - x^*)}{n} \frac{E}{R(T^*)^2} \tag{11}$$

where dx^*/dT^* = change in x at T^*. Since $dT = \phi dt$, eq. 11 may be rewritten as:

$$\frac{dx^*}{dt} = \phi \frac{(1 - x^*)}{n} \frac{E}{R(T^*)^2} \tag{12}$$

Combining eq. 12 with eq. 2 for the special condition $T = T^*$, the following expression for the scan rate is obtained:

$$\phi = An\,(1 - x^*)^{n-1}\,\frac{R(T^*)^2}{E}\,\exp\,(-\,E/RT^*) \tag{13}$$

Taking the logarithm of eq. 13 gives:

$$\ell n\,\phi = \ell n\,A + \ell n\,n + (n - 1)\,\ell n\,(1 - x^*) + 2\,\ell n\,T^* + \ell n\,\frac{R}{E} - E/RT^* \tag{14}$$

Differentiating $\ell n\,\phi$ with respect to $(1/T^*)$, we obtain:

$$\frac{d\,\ell n\,\phi}{d(1/T^*)} = (\frac{n - 1}{1 - x^*})\,(T^*)^2\,\frac{dx^*}{dT^*} - 2T^* - \frac{E}{R} \tag{15}$$

Substituting Eq. 11 into Eq. 15 provides:

$$\frac{d\,\ell n\,\phi}{d(1/T^*)} = -\,[\frac{1}{n}\frac{E}{R} + 2T^*] \tag{16}$$

In this second case, a plot of $\ell n\,\phi$ versus $(T^*)^{-1}$ from several DSC curves will give a straight line with slope $(-\,E/nR)$ when $E/nR \gg 2T^*$.

Results and Discussion

The thermosetting material used in this study was HT424 structural adhesive (Bloomingdale Division, American Cyanamide). This is a complex, glass fiber and aluminum powder filled, epoxy-phenolic system which cures through condensa-

tion and crosslinking reactions (2). The HT424 was stored in a desiccator at −25°C until use. Then ~ 10 mg samples were immediately encapsulated in standard aluminum pans and raised from 300 to 500°K at a controlled rate in a differential scanning calorimeter. An empty aluminum pan and cover were used as a reference. The instrument used was a Perkin-Elmer DSC-1B coupled to a Leeds and Northrup Speedomax W 10 mv recorder. The theory and scope of the DSC is described in detail by Watson and O'Neill (4,5). Power and temperature calibrations were made according to the manufacturer's manual.

The resultant thermograms (see Fig. 1) were then analyzed by the Ellerstein method through eq. 10. The baseline for each trace was obtained by drawing the best smooth curve connecting beginning and ending baselines. The endotherm between 375 and 400°K is believed to be due to cavitation and volatilization (2). It was assumed that the amount of exotherm hidden in this endotherm was negligible and the analysis was done only on the exotherm. The calculations were made utilizing a programmable desk calculator. This enabled the experimenter to fully analyze one DSC thermogram while another was being generated. Details of the computational methods are summarized in Appendix A.

A typical Ellerstein plot is shown in Figure 2. Several spurious points occur at the beginning and end of the exotherm (not shown on graph). These are believed due to inexact baseline assignment. It is evident in Figure 2 that application of eq. 10 produces an effective linearization of the DSC curve of

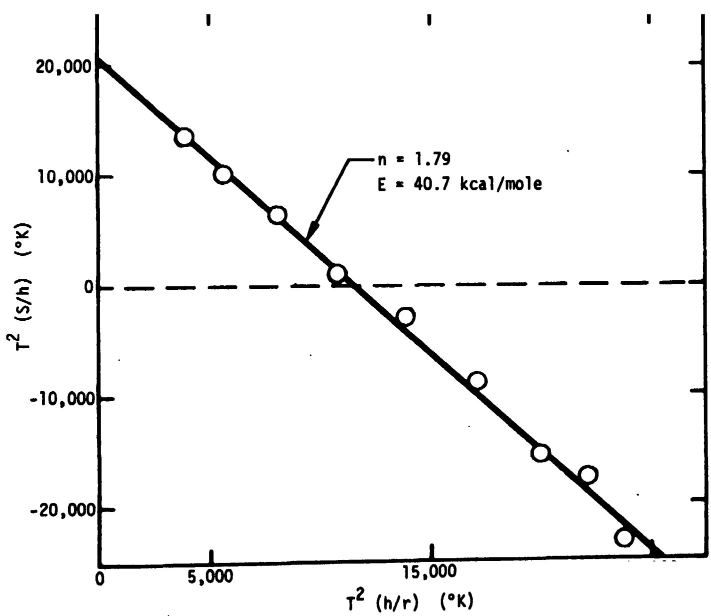

Fig. 2. Ellerstein plot for HT424 (Sample No. 3).

TABLE I

DSC Analysis of Curing in HT424 Epoxy-Phenolic Adhesive

Sample no.	Wt (mg)	ϕ (°K/min)	T^* (°K)	ΔH_p (cal/g)	E (kcal/mole)	n	E/n
1	14.4	5	420	6.29	45.3	1.95	23.2
2	13.2	5	424	4.83	42.9	1.76	24.4
3	9.0	10	434	7.69	40.7	1.79	22.7
4	13.1	10	435	7.56	47.0	2.09	22.5
5	7.9	20	446	8.44	34.3	1.37	25.0
6	12.1	20	445	7.21	39.1	1.49	26.2
7	10.5	40	461	6.97	42.5	1.56	27.2
8	9.3	40	459	7.11	40.5	1.48	27.4
9	11.7	80	480	7.65	41.5	1.53	27.1
10	7.9	80	481	8.15	38.4	1.45	26.5
			Average values:	7.19	41.2	1.65	25.2
			Standard deviations:	± 1.03	± 3.6	± .23	± 1.9
			% Deviation:	± 14%	± 9%	± 14%	± 8%

Figure 1. All DSC scans analyzed in this study display an equivalent linearization by eq. 10. The results of ten DSC experiments are summarized in Table I. A reaction order of $n \simeq 2$ obtained at lower scan rates $\phi = 5$ and 10°K/min is reduced to $n \simeq 1.5$ at the higher rates of $\phi = 20$, 40, and 80°K/min. The average activation energy E = 41.2 kcal/mole from Eq. 10 is comparable to the value E = 38.6 kcal/mole (see Fig. 3) obtained using Eq. 16 where n = 2.0 defines the reaction order. When corrected for the reaction order $n \simeq 2.0$ the apparent activation energy $E^* = E/n = 18.7$ kcal/mole determined in a previous study (2) provides E = 37.4 kcal/mole in close agreement with the determination from eq. 10 and eq. 16 in this analysis of the reaction kinetics of HT424 adhesive.

Summary and Conclusions

The experimental data of Table I shows that the Ellerstein analysis method, as defined here by eq. 10, is insensitive to variations in sample weight. The linearization of the DSC curve of Figure 1 by the Ellerstein analysis, as shown by Figure 2, provides confirmation of the assumptions of eq. 10 that the kinetic order n and activation energy E are independent of the reacted fraction x. Linearization of T^* values, according to the criteria of eq. 16, as shown in Figure 3, confirms the assumption that E and n are substantially independent of scan rate ϕ. It is evident that eq. 10 and eq. 16 provide a new and useful method for investigating the reaction kinetics in either pure polymers or polymer matrix composite systems as typified by the HT424 adhesive utilized in

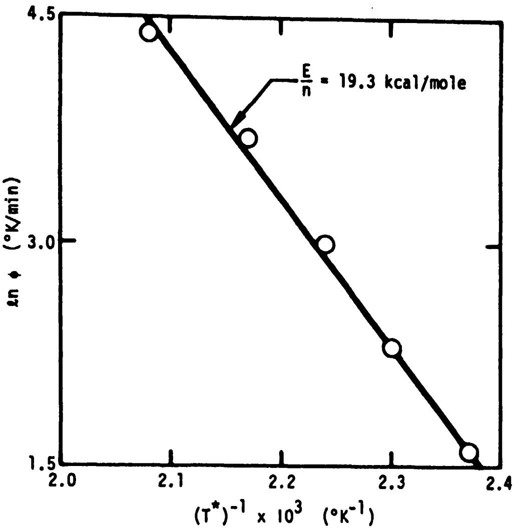

Fig. 3. Correlation of ℓn ϕ versus $(T^*)^{-1}$ for five scan rates on HT424.

this study. In principle, a single DSC scan at a constant scan rate, ϕ, is sufficient to define both the kinetic order, n, activation energy, E, and heat of polymerization, ΔH_p, for a curing system by utilization of eq. 10. In practice, the use of multiple scan rates and a combined analysis by multiple application of eq. 10 coupled with evaluation of scan rate effects in terms of eq. 16, provides a more comprehensive evaluation of the reacting system.

APPENDIX A

Computation for Analysis by the Ellerstein Method

(1) A smooth baseline is drawn on the DSC recording (see Fig. 1) connecting baselines before and after the peak deflection.

(2) Chart values for curve and baseline are taken at equal temperature intervals dT. These numbers, along with dT, range (R), temperature (T), and scan rate (ϕ), are fed into a programmed calculator.

(3) The curve height in chart units is determined by difference and converted to actual height h through the following formula:

$$h(\text{mcal/deg}) = \frac{\text{height (chart units)} \times R\left(\frac{\text{mcal}}{\text{sec}}\right) \times 60\,\frac{\text{sec}}{\text{min}}}{\text{No. chart units full scale} \times \phi\ (\text{deg/min})}$$

(4) Corresponding slopes S are computed from successive heights and dT as follows:

$$S = \frac{h_2 - h_1}{dT}$$

(5) The partial integrals H_p are calculated through the relation:

$$H_p = dT \times \frac{h_1 + h_2}{2}$$

(6) The areas r are found by subtracting successive H_p's from the total integral ΣH_p.

(7) The calculator performs steps 3-6 and displays values for $T^2(s/h)$ and T^2 (h/r) which are then plotted (see Fig.2).

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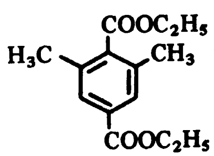
BOOK REVIEWS

Bindung, Struktur und Reaktionsmechanismen in der Organischen Chemie, Ivan Ernest, Springer-Verlag, Wien, 1972. 389 pp. $31.10

The author attempts ". . . to present the current aspects of organic chemistry in a manageable number of pages." In some ways he succeeds, but in many other ways he falls short of the mark. The subject matter is divided into five major subdivisions (Structure of Organic Compounds, General Characteristics and Classification of Organic Reactions, Polar Reactions, Radical Reactions, Multicenter Electron Redistribution Reactions) covered in 389 pages including references and indices. The orbital diagrams are often unclear and difficult to understand because they are too lightly and too compactly drawn. The author index does not allow one to find topics by an author's name since no page numbers are given in the list of references. Space is often wasted by reproducing resonance forms unnecessarily e.g., pp. 84–85. Because of the restriction on space, the treatment of topics such as quantum mechanics and molecular orbital theory suffer badly in the condensation and come through poorly. The organic topics which the author has chosen as being representative are treated clearly and well. The clarity with which the author presents this material makes one regret the author's goal of conciseness. The briefness of the treatment, in some cases, leaves something to be desired, e.g., carbenes on p. 340 are presented in an oversimplified way and no mention is made of metal complexed carbenes as a means of modifying reactivity (copper complexes, Simmons-Smith reaction); the elegant work of Arigoni and Cornforth mentioned on p. 75 should be discussed at greater length to demonstrate its import and not used just to state that hydrogen isotopes are useful in explicating biochemical mechanisms. It would have been most useful to the student-reader had the author applied Sneen's theory on SN1–SN2 mechanisms to a variety of examples (p. 80) rather than just briefly mentioning it.

Among the topics omitted from consideration which, in my opinion, should not have been are: instrumental methods as applied to mechanistic studies (ORD–CD, NMR, MS etc.); other reactive intermediates such as, nitrenes, sulfenes, etc.; mesoionics; fluxional molecules (organometallics as well as bullvalene, etc.); homoconjugation; photochemistry; and others.

Although a sheet of corrections are provided with the text, it does not include all those necessary. The following correct forms should be added to the publisher's list:

183, $C_6H_5C{\equiv}CT$; p. 208,  ; p. 217, $>C^{-}\ Li^{+}$

Spelling errors include p. 343, Nocaradiene; p. *151*, Erwähung.

It strikes me as paradoxical that many of the new undergraduate organic texts often cover 1,000 pages, while Dr. Ernest has condensed so *much into 389 pages. I* do *not have a representative sample of current* German *texts at this level against which to compare this work but, in my opinion, this book does not do its job as well as does, e.g.,* "Advanced Organic Chemistry" by March. *Further, the fact that it is in German and is relatively high-priced* ($31.*10* as of February *1) will probably prevent it from finding much of an* American market.

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Progress in Polymer Science Japan, Volume 3, S. Okamura and M. Takayanagi, Eds., Halsted Press, New York, 1972. 388 pp. $18.50

In this third volume of the series, the first four chapters deal with the mechanisms of chain growth polymerization while the following three are concerned with the properties and structure of macromolecules. While the polymerization reactions discussed in the first two volumes were those taking place by radical mechanisms, the first four chapters here are concerned with ionic and coordination polymerization.

T. Tsuruta, Tokyo University, provides an interesting account of the "Reactivity of α,β-Unsaturated Carbonyl Compounds Towards Nucleophilic Reagents." The description of this reactivity of monomers obtained from a study of reactions and conditions which do not necessarily produce polymers but yield valuable quantitative information is largely a result of the author's own research. A section summarizing and relating these results in terms of anionic initiation, propagation and termination would have been a valuable addition to this chapter.

In Chapter 2, A. Yamamoto and S. Ikeda, Tokyo Institute of Technology, summarize their work on "Coordination Polymerization by Organo-Transition Metal Complexes". This interesting and well written account is concerned primarily with metal complexes other than the Ziegler-Natta type. There are a few omissions, the inclusion of which might have been helpful to a reader not familiar with the field. For example, the mechanism of formation of metal hydrides (p. 55) on treatment of transition metals with AlR_3 or AlR_2OEt was not given. It would have been helpful to point out that complexes containing

M–CH_2CH_3 structures are formed, but especially in the case of Rh and Ru, β-elimination takes place readily and is avoided by using the methyl analog.

S. Okamura, T. Higashimura and T. Miki give a very good account of the "Cationic Polymerization of Trioxane in Solution" in Chapter 3; although the subject matter is rather narrow in scope, a clear presentation of the mechanism of this polymerization is provided.

Chapter 4 is an interesting, well written discussion of "Anionic Alternating Copolymerization" by H. Yuki, Osaka University. This summary is a valuable work for those active in anionic polymerization. In some cases, the explanations of spectra are either not as clear as they could be or are left unexplained. For example, there is not good correspondence between the explanation of the nmr spectrum of the o-methoxy styrene-1,1-diphenylethylene copolymer and the spectrum presented (p. 176–178), the explanation of the species responsible for the electronic spectrum of the polymerization solution (trans-stilbene and styrene, p. 184) is not very satisfying, and the nmr assignments (p. 210–211) for the tactic order in the methyl-α-phenylacrylate and methyl methacrylate copolymer are largely speculation.

The first of the three chapters dealing with the physical properties of polymers is entitled "Relaxation Processes in Crystalline and Non-Crystalline Phases in Polymers". The authors, Y. Wada and R. Hayakawa of the University of Tokyo, present a variety of experimental results on the mechanical and dielectric relaxation of partially crystalline polymers and discuss these results in terms of current theories. Studies of this type are obviously very useful, giving much insight into the nature and importance of the molecular motions occurring in such systems. The basis for some of the models employed in this area, however, is open to serious question, in particular the representation of a partially crystalline polymer as a three-phase system, consisting of crystalline, amorphous, and "intermediate" phases.

The following chapter is on the "Preparation, Characterization, and Viscoelastic Properties of Branched Polymers". The authors have restricted their survey to polymers which have relatively long branches, for example, star-shaped and comb-shaped molecules. A number of ingenious preparative techniques are described, and the solution properties and the viscoelastic behavior of the resulting polymers are described in some detail. One should view with skepticism, however, those arguments based on the authors' assumption that " . . . the conformation of a polymer in an undiluted state must be considerably different from the unperturbed state because of interactions among segments . . . " There is now much experimental evidence contradicting this assumption, including some recent, very definitive neutron scattering results on amorphous, undiluted polymer systems.

In the last chapter of this volume, Y. Kobayashi and T. Isemura of Osaka University discuss "Polypeptides Related to Collagen and Its Triple Helical Structure". The goal of the type of study described here is the elucidation of the dependence of the secondary and tertiary structure of a protein on its primary structure. More specifically, this chapter deals with the experimental

investigation of a series of appropriately chosen polypeptides in an attempt to understand better the triple helical structure of collagen. The syntheses and characterization involved are difficult, but the results presented here seem to be well worth the effort required in such investigations.

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Nonpolluting Coatings and Coating Processes, J. L. Gardon and Joseph W. Prane, Eds., Plenum Publishing Corp., New York, 1973. 272 pp. $17.50

This is a book which might be entitled, "What You Have Always Wanted to Know About Nonpolluting Paints but Didn't Know Where To Look". In many respects, it is an elementary account. Yet in other parts, it contains appropriate techniques utilizing high science. This ambivalence derives from the fact that the book is a collection of papers presented in 1972 at an ACS Symposium on the subject. In one instance, there is a "how to" chapter which describes typical emulsion polymerization, solution polymerization, paint preparation and panel penetration followed by application and test methods relating the results of coatings performance. Then follows an addendum containing the theory of solubility and solution viscosity along with structural formula. The reference to nonpollution aspects is simply the fact that the coatings are free of organic solvents.

In the matter of depurating the air, scientists in the polymer coatings industry are providing four primary approaches to reducing solvent emissions in the industrial application of industrial paints. These are: water based systems; high solids variations of traditional solvent types; powders; and radiation of monomers of oligimers to create coatings upon moving substrates.

The advantaged readers are the engineers of manufacturing companies, technicians, and administrative personnel charged with choosing new coatings which

enable compliance with Federal and State laws. One of the systems (electrodeposition) offers substantial relief in the matter of water disposal problems, namely, ultrafiltration. There is, unfortunately, no coverage of high solids concepts. This is perhaps an appropriate omission since long-term water as a vehicle for the resinous portion of paints will be favored in terms of consummate compliance with future regulations and when one considers the fuel requirements to effectuate afterburning of solvents in catalytical burners.

The work is the most direct source under one cover for the uninitiated coatings user to understand the ramifications of the several types (and hybrids) of aqueous systems: latex (i.e., dispersions), "soluble" (i.e., colloidal dispersions and water solubilized), the hybridized varieties of the latter and finally, electrocoating systems. The separate papers on cross-linking of aqueous systems and coalescing mechanisms for latex types are valuable.

There are extensive literature sources on electrodeposition. In the opinion of the reviewer, the advent of ultrafiltration assured the growth of this application technique by reasons of economy and its contribution to the amelioration of the problems of waste water disposal. The coverage of ultrafiltration principles and operating techniques is excellent and provides in one paper, 203 pertinent references.

Several good vignettes also assist the further description and classification of this book. A chapter on electron beam curing is an excellent assessment but lacks details of experimentation. This is followed by a chapter on electron beam technology, which concentrates upon design critical to optimization of processing. Electrostatic powder methods are covered in both a general overview and also with reference to opacity measurement of films in the range of thickness desired in paint technology.

The term "nonpolluting" in the title must be interpreted in its most liberal context. Probably, the editors whish to convey the impression that the techniques covered, offer relief under most present guidelines and local regulations. In some actual practices, electrodeposition can pollute streams and radiation techniques can pollute the air. This exigency is recognized in the preface.

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Received July 2, 1973

ESR Applications to Polymer Research (Nobel Symposium No. 22), P.-O. Kinell and B. Rånby, Eds., John Wiley & Sons, Inc., New York and Almqvist & Wiksell, Stockholm, 1973. 312 pp. $15.00

This report of symposium proceedings contains 24 papers presented at Stockholm in June 1972, together with a record of the subsequent discussions. The stated purpose of the symposium was to exemplify the many uses of electron spin resonance (ESR) techniques in the various subfields of polymer science. In line with this approach, the papers are reports of experimental work, rather than reviews or introductory treatises.

The application of ESR to polymer research is by no means new, and there were no reports of striking new techniques or methods. Nevertheless, some of the papers contain new information of considerable value. Notable among these are the work of Szwarc on intramolecular collisions between the end groups of hydrocarbon chains, and that of Rånby on copolymerization of vinyl monomers.

The symposium was divided into seven sections. The section titles are: "Initiation Reactions," "Polymerization Reactions," "Crosslinking Reactions," "Photochemical Degradation and Oxidation," "Mechanical Fracture of Polymers," "Molecular Orbital Calculations," and "Molecular Motion in Polymers".

The editing of the volume is poor. The papers and discussions do not appear to have been reviewed and consequently contain numerous errors, omissions, and misprints at all levels of seriousness. Some examples chosen at random are as follows: On p. 26, ordinary hydrocarbons are assigned a g-factor of 2.02, rather than 2.002. On pp. 44–47, very complex ESR spectra are displayed without any accompanying justification of the assignment of the spectra to certain radicals. On p. 218 there is a discussion of the production of chain end radicals by means of a low-high energy process in PTEE which fails to refer to the pioneering work of Siegel and Hedgepeth [J. Chem. Phys., 46, 3094 (1967)]. On p. 268, the symbols M and τ_i are introduced without any explanation of their significance. On p. 307, some experimental results on the g-factor of the peroxy radical in PTFE are set forth by one of the discussants. On the basis of spectra essentially identical with those which are generally accepted he concludes that this radical has an anisotropic g-factor. Since the g-factor of this radical is generally considered to have axial symmetry, one could wish for the presentation of further evidence. Finally, in order to find details of the experimental techniques used earlier publications must be consulted since many of the papers are extensions of previously published work and the papers are not complete in themselves.

On another level, the editors have failed to concern themselves with the English of contributors whose native language is not English. Errors which are perfectly understandable in oral presentations should really not be perpetuated in print. The following are examples of this: On p. 188, "It was found that the ratio of radical formation is linear to the light intensity when the light intensity is weaker." On p. 275, "Irradiation is made for trapping of the free radicals."

A volume of symposium proceedings should serve a purpose which could not be served as well by the standard journals. If it concerns itself with original contributions, it should in some sense or other convey some overall theme or spirit. In this case, the intent was to demonstrate the many ways in which ESR can be applied to polymer science. This goal is achieved only in part. Individual polymer scientists may well find some articles in this volume of great interest to them.

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Received July 10, 1973

Stress Analysis of Polymers, J. G. Williams, Halsted Press, New York, 1973. 275 pp. $16.95

In this clear, careful, and ordered presentation, the author achieved his objective of providing a self-contained course in stress analysis applicable to polymeric solids. The chapter titles correctly describe the areas covered: (1) "The Analysis of Stress and Strain," (2) "Time Independent Behavior," (3) "Time Dependent Behavior," (4) "Problems Involving Bending," (5) "Problems with Axial Symmetry," and (6) "Problems of Stress Concentrations and Cracks". The mathematical level is limited, and tensor or matrix representation is not used. The derivations are all carried out in enough detail so that each stage of the development is very easy to follow.

Will the book appeal to the groups at which the author claims, in the introduction, to aim, that is, the engineers with "little experience of large strain behavior and time dependence" and the "many chemists" who "need to understand stress analysis"? I doubt it. Nowhere in the book are any physical data or experimental results presented. The practicing polymer engineer or chemist will feel very much overwhelmed in this sea of formal stress analysis without the flotsam and jetsam of experimental realities to buoy him up. The average reader would certainly need to supplement his study of this book with some volume, such as Nielsen's "Mechanical Properties of Polymers", which emphasizes the experimental realities and practical complications of polymer systems. This is particularly important because of the very limited bibliography provided by Williams. It is also worth noting that beyond a discussion of sandwich beams there is no consideration of the very active area of polymeric composite materials. On the theoretical side, for the reader with a taste for stress analysis and a need to read current work in the field, the book provides a detailed basis from which a transition to tensor and matrix representation should be

very easy. The reader might thus well proceed from this book to an undergraduate text such as Long's "Mechanics of Solids and Fluids".

In summary, this book fills a gap which exists in the formal training of many polymer engineers and most polymer chemists. Considerable input beyond this book would be necessary before these engineers and chemists could usefully attack problems of stress analysis of polymers.

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Received July 13, 1973

Friction of Polymers (Russian), Nauka, Moscow, 1972. 204 pp. Rubles 0.90

The four authors of this slim volume (V. A. Belyi, A. I. Sviridenok, M. I. Petrokovets, and V. G. Savkin) are not mentioned on the title page. They have no reason to be ashamed of their performance because their fundamental idea—that knowledge of the viscoelastic properties of a polymer is needed to understand its frictional behavior—is sound. Unfortunately this idea alone is unsufficient to build up a workable theory of friction.

First, the popular hypotheses are discussed; none are accepted, but only lukewarm criticism is permitted to surface. In the second chapter, a brief review of the experimental data on polymer friction, with and without a lubricant, is given, and the mechanisms of molecular adhesion are sketched in the customary manner. It is not clear to the reviewer whether the inclusion of chapters 3 and 5 (62 pages together) on the rheological properties of polymeric materials and on polymer structure is justified here; presumably, the authors' contributions to these areas of knowledge were felt to be a reason enough.

Chapter 4 deals with "Formation of Real Interface Area during a Viscoelastic Contact". It is assumed again and again that this area is of greatest importance to friction. The calculation is said to be the first for viscoelastic bodies. Unfortunately it still gives only the geometrical area which may be very much greater than that along which no material is present between the atoms of the slider and those of the support. The theoretical results are compared with experimental data on the optical contact area, but optical contact as well is very different from the atomic one. To achieve the deformation resulting in the contact area calculated by the authors, obviously work must be expended, and this work must be a part of (or equal to) the frictional work; but this necessity is not discussed.

The last two chapters treat polymer bodies as sandwich-like structures; the surface layers (which are deformed first) are supposed to have mechanical properties different from those of the bulk. To the reviewer this approach appears promising and the data so far obtained appear valuable. The list of references includes 289 Russian and 116 foreign publications.

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Received August 8, 1973

Free Radicals, Volume 1, Dynamics of Elementary Processes, Jay K. Kochi, Ed., Wiley-Interscience, Inc., New York, 1973. 713 pp. $37.50

The field of free radical reactions is now too complex and the literature too voluminous for any single author to hope to produce a comprehensive review in a single volume. The next best solution is the multiauthor-multivolume treatise, and Dr. Kochi has been unusually successful in both his balance of topics and selection of authors. The contents, taken together with those of Volume II (which is also now available) cover most of the areas of free radical reactions of current research interest.

A more detailed view of contents is best provided by an abbreviated list of chapter headings and authors: "Rate Processes in the Gas and Liquid Phases" by J. A. Kerr and K. V. Ingold, respectively; "Decomposition of Peroxides and Azoalkanes" by T. Koenig; "Cage Effects" by T. Koenig and H. Fischer; "Trimethylene" by R. G. Bergman; "Chemically Induced Dynamic Nuclear Polarization" by N. R. Ward; "Reactivity in Hydrogen Atom Transfer" by G. A. Russell; "Free Radical Rearrangements" by J. W. Wilt; Electron Transfer of Organic Anions" by J. F. Garst; "Substitution at Metal Centers" by A. G. Davies and B. P. Roberts; and "Redox Reactions of Radicals and Metal Complexes" by J. K. Kochi. All are well done (as might be expected from the authors involved) and although sections vary in depth and completeness, they show little overlap and are at a level which should be valuable to both specialists and nonspecialists. In all, emphasis is primarily on reaction mechanism, with generally adequate attention to experimental methods and occasional mention of synthetic application.

In summary, this is certainly the most comprehensive and up to date treatise on free radical reactions available and will undoubtedly be frequently cited for many years. My only negative comments are that the editors have unfortunately put all references at the end of chapters; this is bad enough for journal

references when authors are rarely mentioned in the text, but is even more frustrating to the reader when comments are put there as well! Also, readers of this journal will find little attention paid to the role of free radicals in polymer chemistry, an area which played an extremely important role in the development of free radical chemistry, but now receives little academic attention.

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Received July 26, 1973

ANNOUNCEMENTS

International Symposium on Macromolecules

Circular 1 on an International Symposium on Macromolecules, under the sponsorship of International Union of Pure and Applied Chemistry (IUPAC), to be held in Rio de Janeiro, Brazil, July 26 to 31, 1974, is available under request from:

Prof. Eloisa B. Mano
Academia Brasileira de Ciências
C.P. 229, Rio de Janeiro, Brasil.

A charter flight is being organized starting in Europe. Information on this flight is available from:

Prof. G. Kossmehl
Institute of Organic Chemistry,
Free University of Berlin
Thielallee 63-67 – 1, Berlin 33
West Germany

A charter flight from the United States is being arranged through

Dr. Henry Friedlander
Union Carbide Research Institute
P.O. Box 278
Tarrytown, New York 10591.

Fall Meeting of the Textile Quality Control Association

The meeting will take place on September 20-21, 1973, at the Holiday Inn No. 6, Charlotte, North Carolina.

For further information, write to William J. Martin, P. O. Box 147, Clemson, South Carolina 29631.

Symposium on People, Products, and Processes

The Symposium on People, Products, and Processes will be held by the Cleveland Society for Paint Technology on September 20-21, 1973, at the Cleveland Engineering Center, Cleveland, Ohio.

For further information, write to Earle F. Sickels, Body Bros., Inc., 214 Northfield Road, Bedford, Ohio 44146.

National Technical Conference of the American Association of Textile Chemists and Colorists

This conference will be held at Chalfonte-Haddon Hall, Atlantic City, New Jersey, on September 20-22, 1973.

For further information, write to George P. Paine, American Association of Textile Chemists and Colorists, P. O. Box 12215, Research Triangle Park, North Carolina 27709.

Regional Technical Conference of the Society of Plastics Engineers

This conference will take place on September 24-25, 1973, at the Cherry Hill Inn, Cherry Hill, New Jersey.

For further information write to Dr. Boris Gutbezahl, Rohm and Haas, P. O. Box 219, Bristol, Pennsylvania 19007.

Fall Meeting of the American Chemical Society Rubber Division

This meeting will take place at the Denver Hilton Hotel, Denver, Colorado, on October 9-12, 1973.

For further information write to Dr. H. W. Day, Du Pont Company, 140 Federal Street, Boston, Massachusetts 02110.

Fifth European Symposium on Food–Rheology in Food Processing and Food Quality

This symposium will take place on October 10-15, 1973, at Zurich, Switzerland. For further information, write to Gesellschaft Deutscher Chemiker, D–6000, Frankfurt (M), Posttach 119075, Germany.

Fall Seminar on World Problems, Standards, and Technology

The Adhesive and Sealant Council will hold its fall seminar on October 20-31, 1973, at the Hotel Bonaventure, Montreal, Quebec, Canada.

For further information, write to R. M. Stansel, ASC, 1410 Higgins Road, Park Ridge, Illinois 60068.

Paper Synthetics Conference

This conference will be held at the Sheraton-Jefferson Hotel, St. Louis, Missouri, on October 22-24, 1973.

For further information, write to W. B. Manning, TAPPI, 1 Dunwoody Park, Atlanta, Georgia 30341.

Forty-Fourth Annual Meeting of the Society of Rheology

This meeting will be held on October 28-31, 1973, at the Sheraton-Mount Royal Hotel, Montreal, Quebec, Canada.

For further information, write to H. P. Schreiber, Department of Chemistry, McGill University, Montreal, Quebec, Canada.

IUPAC International Symposium on Macromolecules

The meeting will be organized by Instituto de Plásticos y Caucho and it will take place at the Palacio de Congresos (Congress Palace) of Madrid, Spain, from Sunday, 15th, September to Friday, 20th September, 1974.

Emphasis will be given to the relationship between chemical structure and properties of polymers.

The programme will be arranged in four main Sections and main lectures will be given as a separate series.

Each section will consist of a limited invited lecturers and contributed papers.

The Scientific Programme Committee will consider papers of interest in relation to the following topics:

1. New developments in polymerization.
2. Chemical modifications and reactions on polymers.
3. Properties in amorphous and crystalline polymers.
4. Influence of structure on technical properties.

The main lectures will be published in the IUPAC official journal "Pure and Applied Chemistry" and the Symposium Committee will publish the preprints of all contributed papers. These preprints will be available to all registered participants.

The invited lectures will be given in English. Contributed papers may be presented in any language, but the organizers suggest that speakers should use

preferably English or French that is commonly understood by most participants. Simultaneous translation will not be arranged.

Those planning to attend the Symposium are requested to complete and return the preliminary registration form as soon as possible and not later than October 1st, 1973.

This will ensure receipt of Circular 2 which will be distributed in November, 1973. In order to ensure that sufficient hotel accommodation is available the organizers would be grateful to know whether participants expect to be accompanied by their families during their stay in Madrid.

Circular 2 will include further information about the programme, Symposium fees, deadline and instructions for the preparation of preprints, final registration details, information on travelling and accommodation facilities, social events, etc.

Reservation will be available in hotels in the city through the Accomodation Office. Special travel arrangements and the official travel agents for the Symposium are being negotiated. Full details will be available in the Second Circular.

The Executive Committee consists of Prof. J. Fontán, Chairman, and Prof. J. G. Fatou, General Secretary.

Inquiries and other correspondence concerning the Symposium should be addressed to:

Prof. J. G. Fatou
Instituto De Plasticos Y Caucho
Juan de la Cierva, 3 Madrid-6 (Spain)

The *Journal of Polymer Science* publishes results of fundamental research in all areas of high polymer chemistry and physics. The *Journal* is selective in accepting contributions on the basis of merit and originality. It is not intended as a repository for unevaluated data. Preference is given to contributions that offer new or more comprehensive concepts, interpretations, experimental approaches, and results.

In addition to meeting these standards for excellence and significance, manuscripts for the *Polymer Letters Edition* must exhibit a special degree of novelty and timeliness that warrants speedy publication, even in brief preliminary form. Short contributions that do not in the opinion of the editors meet this test, but are otherwise acceptable, will be published as *Notes* in the *Polymer Chemistry* or *Polymers Physics Editions*.

Three copies of every manuscript are required. They may be submitted to the appropriate editor: C. G. Overberger (chemistry, physical organic chemistry), Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, or T. G Fox (physics, physical chemistry), Mellon Institute, Pittsburgh, Pennsylvania 15213. Alternatively, manuscripts may be submitted through the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201. All other correspondence should be addressed to Periodicals Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016.

Detailed instructions on preparation of manuscripts are given frequently in the *Polymer Chemistry* and *Polymer Physics Editions*.

Polymer Letters Edition

September 1973 Volume 11 Number 9

JOURNAL OF POLYMER SCIENCE

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Journal of Polymer Science: Polymer Letters Edition

The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition*, monthly; *Polymer Physics Edition*, monthly; *Polymer Letters Edition*, monthly; *Polymer Symposia*, irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition, Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

POLYMER LETTERS EDITION VOL. 11, PP. 555–562 (1973)

TRANSPARENT HIGH DENSITY POLYETHYLENE FILMS CRYSTALLIZED UNDER ORIENTATION AND PRESSURE

Introduction

Transparent, oriented, high-density polyethylene films have been produced by crystallization under the combined orientation and pressure effects during extrusion through a slit die with the Instron Rheometer. Crystallization induced under extrusion conditions, previously studied in some detail (1–11), resulted in transparent polyethylene strands having a microfibrillar structure organized into columns and ribbons (3,6). The unusually high strand melt transitions, tensile properties, and degree of transparency were attributed to uniaxial orientation and the presence of extended chain crystallites, evidenced by selected area electron diffraction patterns from 5000 Å long

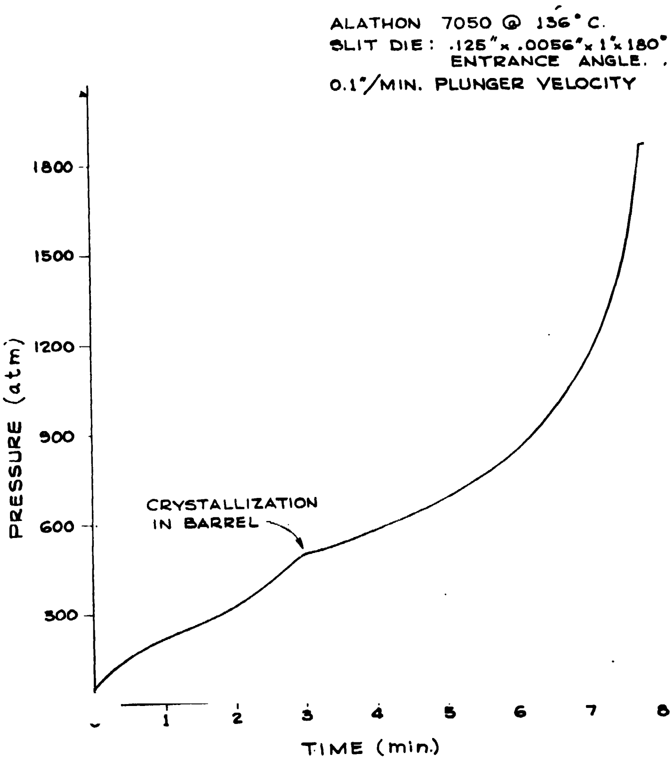

Fig. 1. Instron pressure accompanying crystallization in a slit die.

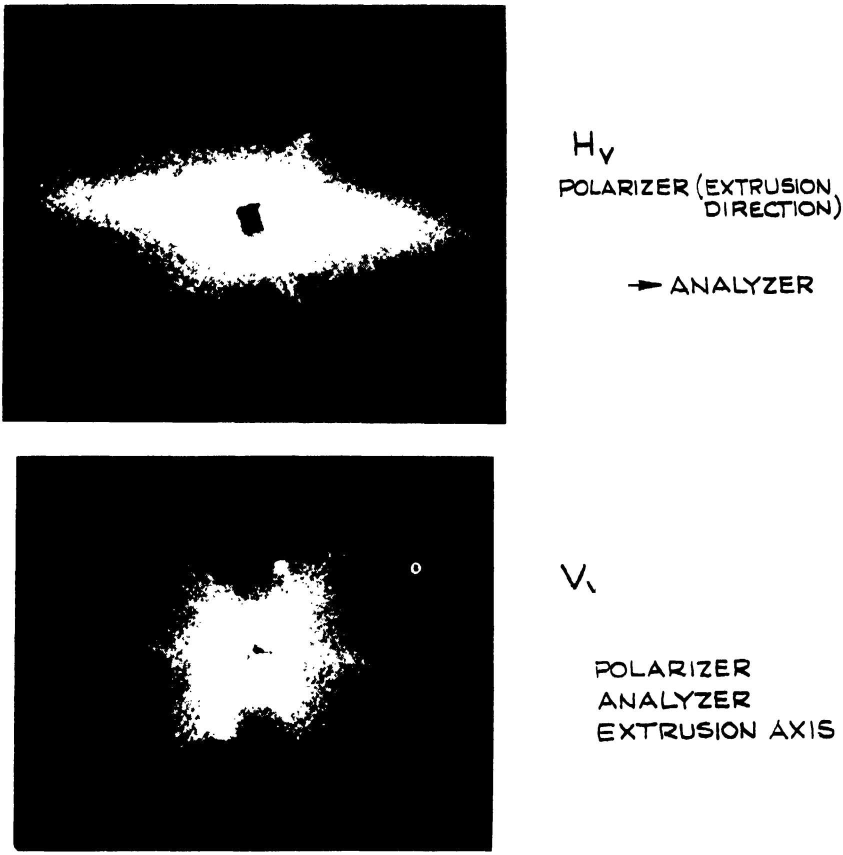

Fig. 2. H_V and V_V small angle light scattering patterns from the transparent film.

strand microfibrils (6). The transparent film morphologies reported here were investigated with electron microscopy, x-ray, light scattering, and calorimetry techniques; the results are compared with the transparent strand structure.

Crystallization Procedure

For both the Instron-crystallized strands and films, the structure results from pressure-induced crystallization under the severe orientation effects of an extensional velocity gradient in the capillary or slit die entrance region. The high density polyethylene (Alathon 7050) films are crystallized at temperatures near the atmospheric melt transition by forced extrusion of a semicrystalline plug from the 0.375″ diameter Instron barrel into a 0.125″ X 0.0056″ X 1″ long, flat land (180° entrance geometry) slit die. A typical Instron pressure trace accompanying film formation is noted in Figure 1, where the second-

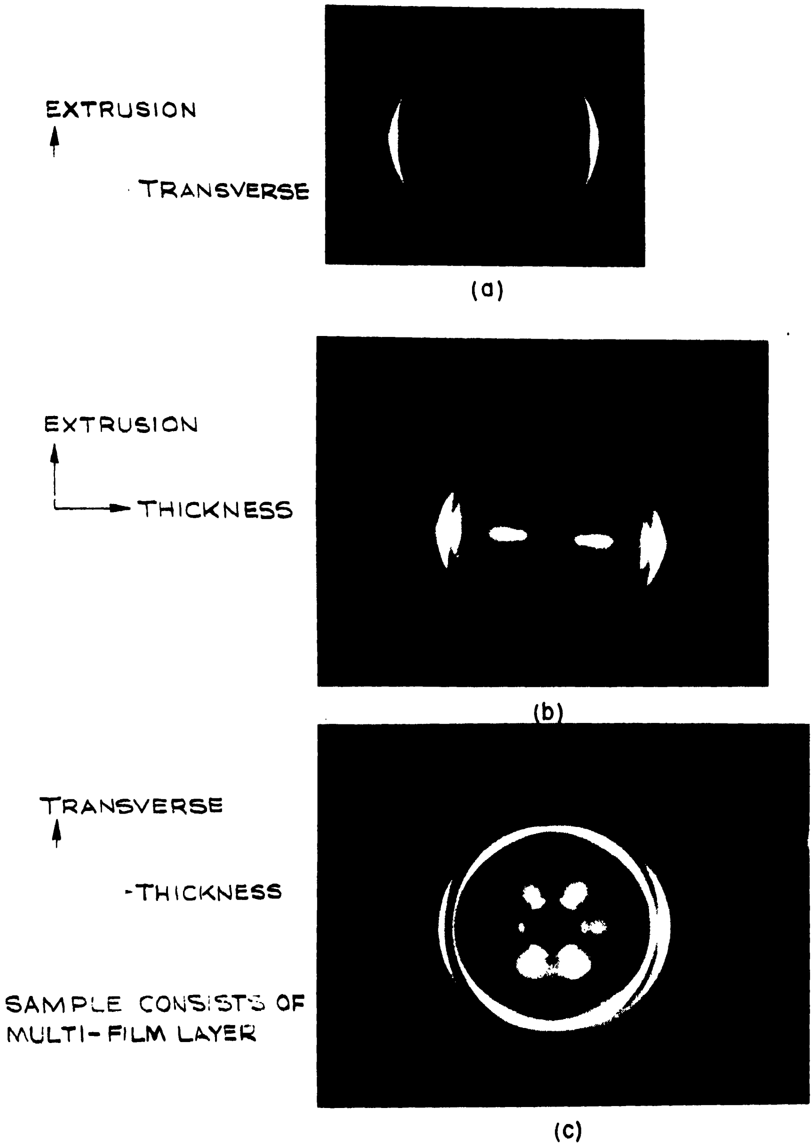

Fig. 3. Wide angle x-ray patterns with the incident beam parallel to the film: a. thickness direction; b. transverse direction; and c. extrusion direction.

ary maximum at 520 atm is attributed to the volume decrease accompanying massive crystallization in the rheometer barrel. The pressure dependence of the polyethylene fusion temperature is 0.02°C/atm (12); thus, crystallization

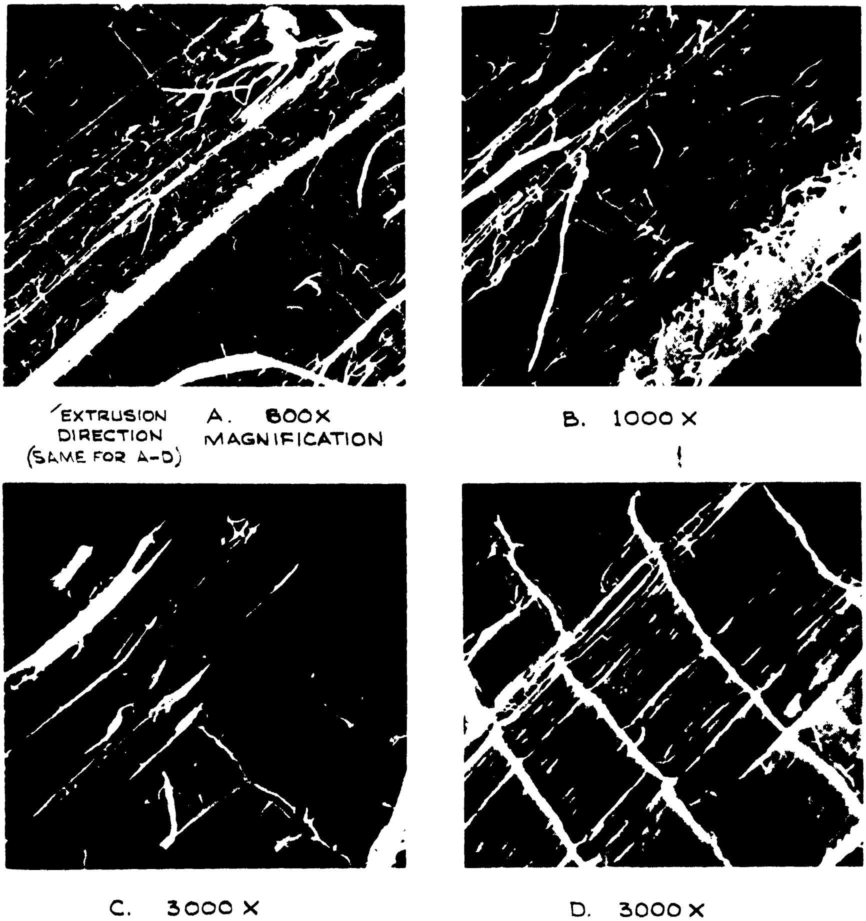

Fig. 4. Scanning electron micrographs of the transparent film.

is to be expected at the 136°C Instron temperature due to the 16°C of supercooling from the 520 atm pressure. This calculation neglects entropy effects due to orientation under the velocity gradients and assumes a 142°C equilibrium melt transition at one atmosphere pressure (13). The transparent film length increases continuously as a function of time at 1900 atm pressure, hence is produced from forced extrusion of the semi-crystalline reservoir plug (4).

Discussion

As evidenced by the accompanying light scattering (Fig. 2), x-ray (Fig. 3), and electron micrographs (Figs. 4 and 5), the transparent film morphology consists of a series of platelets, composed of ribbons or rod-like elements

Fig. 5. Scanning electron micrograph of the film fibrillar structure.

oriented normal to the thickness direction and parallel to the extrusion axis. The H_V small angle light scattering (SALS) pattern in Figure 2 clearly suggests a nonspherulitic morphology, for the conventional SALS four-leaf clover pattern showing a maximum as a function of radial angle (14) is absent. Based on previous SALS interpretations of transparent quench-rolled polyethylene patterns (15,16) and from the theory of anisotropic rod scattering (17), the Instron-crystallized films SALS patterns in Figure 2 imply a rod or ribbon texture preferentially oriented in the extrusion (machine) direction.

Three dimensional orientation in the Instron transparent film crystal structure is evidenced from the Figure 3 wide angle x-ray (WAXS) patterns interpreted as follows (assuming an orthorhombic unit cell): 110 and 200 plane equatorial maxima (Figure 3a and b) indicate c-axis orientation in the extrusion direction, whereas the 200 reflection, most pronounced in Figures 3b and 3c, implies preferential a-axis alignment in the thickness (normal) direction (with slight a-axis orientation in the extrusion direction denoted by the relatively weak meridianal 200 reflection in Fig. 3a). It follows that b-axis orientation is in the transverse direction. Biaxial orientation clearly exists with respect to the extrusion axis, as indicated by the azimuthal dependence of Figure 3c where the beam is along the extrusion axis. This is in contrast to the crystalline orientation of the transparent Instron-crystallized strands (5) which display uniaxial c-axis orientation in the extrusion direction with random align-

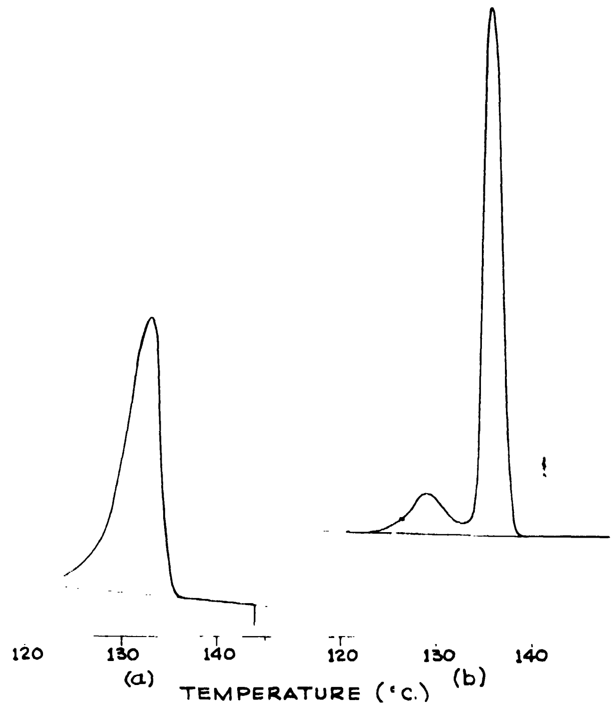

Fig. 6. DSC fusion traces of the instron-crystallized polyethylene: a. opaque plug from reservoir, T_m = 132.8°C, ΔH = 48.9 cal/g; b. transparent film from die, T_m = 136 and 129.2°C, ΔH = 53.7 cal/g.

ment of the a- and b-axes normal to this direction. In addition, a "swirl" or pinwheel-like WAXS pattern, observed when the x-ray beam passes through the upper or lower half (thickness) of a single film, suggests a parabolic orientation profile existing through the thickness direction (observed previously for cold-rolled polyethylene to decrease from the center of the film thickness to its surface (18-20)). This parabolic crystal orientation gradient as well as the crystal unit cell alignment in the film may well result from the longitudinal velocity gradient varying from a maximum in the thickness center to zero at the die walls. This extensional gradient in the extrusion direction results from acceleration of the material forced from the 0.71 cm^2 Instron reservoir area into the 0.0045 cm^2 rectangular slit. Orientation and density fluctuations are reduced as crystallization occurs under the shear and extensional velocity gradients, hence the exceptional transparency of the Instron-crystallized films. Also of interest in the WAXS patterns is a weak reflection observed at a diffraction angle less than that of the 110 plane, indicating the presence of a second crystal structure (possibly monoclinic) commonly noted in polyethylene crystallized under compressive strain (5,21,22).

Representative scanning electron micrographs of film sufaces resulting from

fracture under liquid nitrogen are shown in Figure 4. Note the ridge-like structures aligned along the film transverse direction. These may result from "stick-slip" extrusion into the die or possibly a post-extrusion annealing phenomenon. Higher magnification in Figures 4b–4d reveals a series of ribbons aligned parallel to the flow direction and having their width and thickness dimensions parallel to the slit die width and thickness, respectively. Note also the microfibers approximately 1000 Å in diameter extending laterally between the ribbons. These microfibers may well be the basic component of the ribbons, as evidenced by the fibrillar nature of the Figure 5 sample surface that has undergone a torsional deformation during fracture.

The oriented, pressure-induced crystal structure of the transparent film is significantly different from that of the pressure-induced crystal structure in the Instron barrel, e.g., note the differential scanning calorimeter (Perkin Elmer DSC-1) traces in Figure 6 indicating a 132.0°C melt transition for the opaque plug from the reservoir as compared with the distinctly unusual dual peak fusion trace of the transparent film (136.0°C and 129.2°C). Previous fusion studies of transparent strand samples exposed to various radiation levels (prevents molecular motion leading to crystal annealing or reorganization during fusion) indicated that the higher melting peak does not result from melting followed by recrystallization during the DSC heating cycle (7). Indeed, the film 136°C and 129°C fusion peaks suggest the existence of two different crystalline aggregates that can be attributed to either two different crystalline unit cells, two different degrees of crystalline imperfections or strain, or to the presence of both extended chain and chain folded crystallites (7,23,24).

Conclusions

The high degree of c-axis crystal orientation and the fibrillar or ribbon-like texture are common to both the Instron-crystallized transparent strands (5,6) and films. However, for the slit die the plane nature of the extensional velocity gradient in the die entrance region is believed to produce a further organization of these ribbons and fibrils into a series of planes with the crystallographic c-axis preferentially oriented in the extrusion direction, the a-axis in the thickness direction, and the b-axis along the transverse direction. Only uniaxial c-axis orientation is observed with the strands (5). The DSC and x-ray data presented are consistent with the presence of two crystalline unit cells (possibly monoclinic as well as orthorhombic) and two crystal growth mechanisms (extended chain and chain-folded). These conclusions are in agreement with earlier studies of the strand morphology (3-5).

We are grateful to Professor R. S. Porter (University of Massachusetts) for graciously providing the polyethylene sample and the slit die. In addition, R. D. Ulrich and G. Claver, both of Monsanto Company, provided the essential SEM micrographs. This morphology study has been completed with the encouragement and support of J. H. Saunders and R. L. Ballman (Monsanto).

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Received June 21, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 563–568 (1973)

THE YIELD LOCUS OF POLYCARBONATE

Introduction

The shape of the yield locus is known for few polymers, yet it is a prerequisite for the analysis of plastic deformation processes. Experimental studies have been of two main kinds, first a single mode of loading, such as a tensile test, has been conducted under a variable superimposed hydrostatic pressure, and second the shape of the plane stress section of the yield surface has been examined. The first kind has shown that the yield surface for many polymers tapers towards the hydrostatic axis in the direction of increasing hydrostatic tension; in particular this is true for polycarbonate (1), (2). The second kind has shown that a pressure modified von Mises yield criterion is obeyed by PVC (3) and polymethylmethacrylate (4). Since there is no reported data for polycarbonate, we have investigated the plane stress section of its yield locus.

Theory

The von Mises yield criterion is that for yield to occur:–

$$J_2 = K^2$$

where J_2 is the second invariant of the deviatoric stress tensor, and K is the pure shear yield stress. One simple pressure modification suggested by Drucker (5) is:–

$$J_2^{1/2} + \left(\frac{3}{2}\right)^{1/2} \mu p = K \qquad (1)$$

where the hydrostatic pressure is related to the principal stresses σ_1, σ_2, σ_3, by $p = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$. μ is a material constant. In a plane stress situation this becomes the curve:

$$\sigma_1^2\,(1 - C^2) + (2CD - \sigma_2 - 2C^2\sigma_2)\sigma_1 + (\sigma_2^2 - C^2\sigma_2^2 + 2CD\sigma_2 - D^2) = 0 \quad (2)$$

where $C = \mu/(2)^{1/2} = (\sigma_C - \sigma_T)/(\sigma_C + \sigma_T)$, $D = (3)^{1/2}\,K = 2\sigma_C\sigma_T/(\sigma_C + \sigma_T)$ and σ_C and σ_T are the yield stresses in uniaxial compression and tension, respectively.

If biaxial stresses, σ_1 and σ_2, are applied to produce plane strain deformation in the 1, 2 plane, then the condition that the plastic strain increment is normal to the yield surface in 3-dimensional stress space means that the yield surface is perpendicular to the 3-direction at the point $(\sigma_1, \sigma_2, \sigma_3)$. If a sim-

ple von Mises yield criterion is assumed then the corresponding plastic flow rules are the Levy-Mises equations (6), and the plastic strain increment in the 3-direction is given by:

$$d\epsilon_3^p = \frac{2}{3}\, d\lambda\, [\sigma_3 - \frac{1}{2}(\sigma_1 + \sigma_2)]$$

where $d\lambda$ is a constant. Since $d\epsilon_3^p$ is zero:

$$\sigma_3 = \frac{1}{2}(\sigma_1 + \sigma_2).$$

For a material having the yield criterion of eq. (1), there should be a volume dilation on yielding. If, however, this is ignored, and the Levy-Mises equations assumed to apply, then points representing yielding in the 1, 2 plane will lie on a generator of the conical yield surface, and a plot of the σ_1 component versus σ_2 will have a gradient $(1 + \mu)/(1 - \mu)$.

Mechanical Tests

'Makrolon' polycarbonate sheet of 3 or 5mm thickness, manufactured by Bayer, was used. Five types of sample were prepared: a uniaxial tensile sample of 13mm width and 80mm gauge length, a plane strain tension sample 40mm wide and 40mm long made by machining a 1.5mm deep groove of 9mm radius of curvature on each side of a 5mm sheet, uniaxial compression sample of dimensions 5mm X 5mm X 10mm, a plane strain compression sample 5mm X 25mm X 20mm, and plane strain deformation sample 5mm X 3mm X 50mm. These were annealed in air at 160°C for 30 minutes to remove any initial anisotropy, then either rapidly cooled in air, or given a further four hours at 135°C (the glass transition temperature is 145°C) before cooling. This latter treatment is known (7) to increase the uniaxial tensile yield stress by about 15%.

These samples were strained in a TT/CM Instron machine at 23°C and 50% R.H. in an environmentally controlled room. The strain rate was adjusted so that yielding (determined by the initial maximum in the load-deformation curve) occurred after 100–150 sec. In the plane strain tension sample, the polymer is constrained to neck at 90° to the tensile stress, and the plastic strain in the width direction is only −0.025 compared with −0.45 in the thickness direction. The uniaxial compressive yield stress was measured using polished steel anvils sprayed with fluorocarbon lubricant. The plane strain compressive yield stress was obtained using a device similar to that described by Ford (8) with lubricated anvils 6mm wide and 50mm long. Since this device measures the true yield stress, this was converted to the engineering yield stress by dividing the extension ratio at yield, to be comparable with the other engineering yield stress data measured.

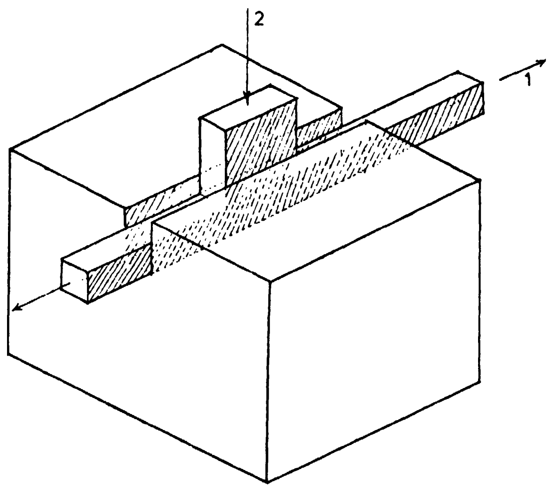

Fig. 1. Device for plane strain deformation under triaxial stress.

The plane strain deformation device shown in Figure 1 was used to determine the engineering yield stress under triaxial stress conditions. A constant tensile stress was applied in the 1 direction on a sample 3mm wide and 5mm high, while the Instron crosshead compressed the specimen in the 2 direction with an anvil 20mm long. In this device tensile stresses greater than 58 MNm^{-2} could not be used otherwise yielding occurred in tension before compression began. The constraining stress σ_3 must give rise to frictional forces in the 1 and 2 directions, but these were assumed to be negligible with the use of fluorocarbon lubricant.

Results

Figure 2 shows the yield locus determined for samples rapidly cooled from 150°C in plane stress conditions, i.e., points for uniaxial tension and compression, and two lines which the yield locus must touch for plane strain tension and compression. For these latter, the stress in the constrained direction is unknown, whereas that in the remaining direction is assumed to be zero. Also shown is the engineering yield stress data of Whitfield and Smith (9) who performed tension-torsion tests on thin walled cylinders of polycarbonate which had been cooled overnight after annealing at 160°C. Unfortunately they assumed that hydrostatic pressure does not affect the yielding of polycarbonate, and, therefore, when their data was projected onto the Deviatoric (π) plane it had a 3-lobed hypotrochoidal shape (assuming the material is isotropic). Projecting their data back onto the σ_1 σ_2 plane gives the points in the fourth quadrant in Figure 2. (n.b. their data in the π-plane is multiplied by an erroneous extra factor of $(2)^{1/2}$). Also shown in Figure 2 is eq. (2) with the parameters C = 0.138 and D = 65.9 MNm^{-2}.

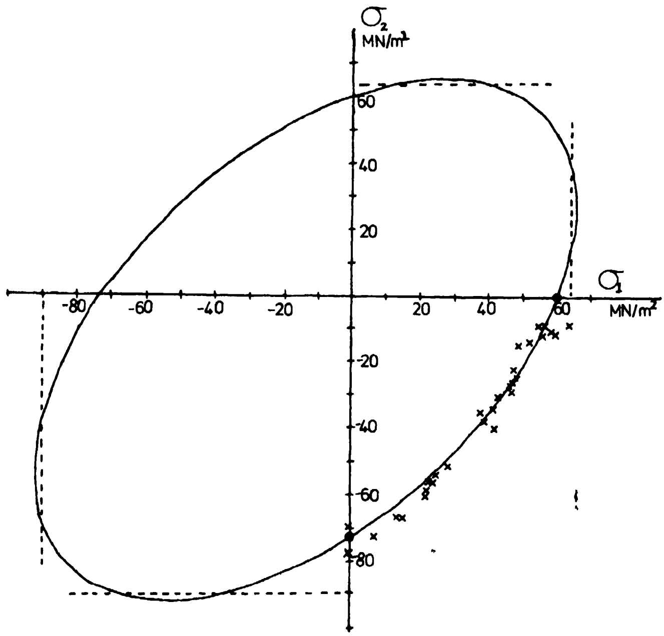

Fig. 2. Plane stress yield locus for polycarbonate. 0 and .....: the authors' data; X: data of reference (9); solid line: eq. (2) with C = 0.138, D = 65.9 MNm^{-2}.

The data for plane strain deformation under triaxial stress conditions of samples annealed at 135°C is shown in Figure 3. With the necessary assumptions to determine the magnitude of σ_3, the gradient of the straight line fitted by least squares to the data implies that $\mu = 0.028$. The point on this line representing pure shear stress is $\sigma_1 = -\sigma_2 = 47$ MNm^{-2}. The respective engineering yield stresses for the annealed samples in uniaxial tension, plane strain tension, uniaxial compression and plane strain compression were 68, 81, 81 and 101 MNm^{-2} with standard deviations of $\pm 1 MNm^{-2}$. The data for the annealed polycarbonate could be fitted by eq. (2) with C = 0.064 and D = 75 MNm^{-2}.

Discussion

The inclination of a generator of the supposedly conical yield surface to the hydrostatic axis was measured in the plane strain deformation experiment as $\mu = 0.03$. This experiment covers the limited hydrostatic stress range of −300 to +60 Bars and has unknown frictional errors. Analysis (2) of the variation of the true tensile yield stress with hydrostatic stresses between −8000 to 0 Bars gave $\mu = 0.072$ and recalculations in that paper of earlier less extensive data (1) gave $\mu = 0.047$. Thus our result is in agreement with better published data.

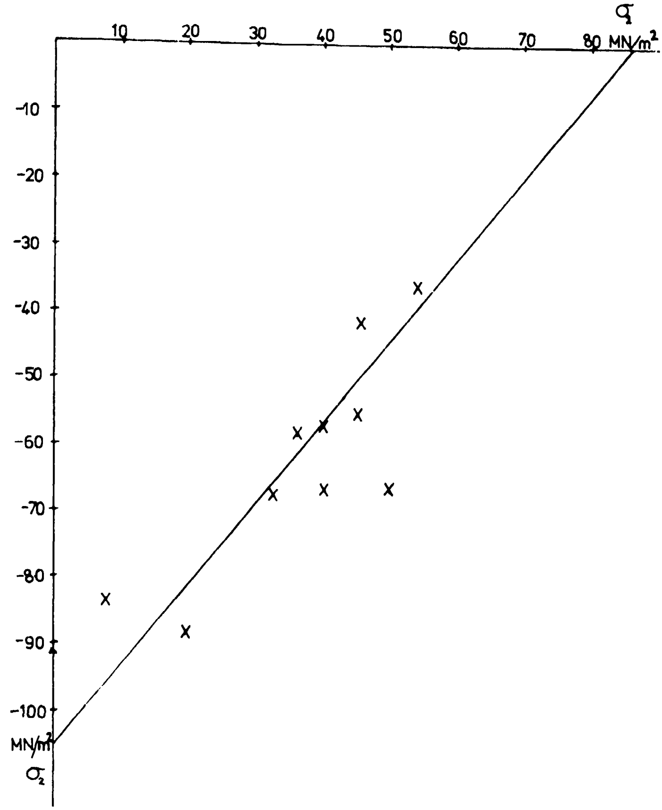

Fig. 3. σ_1 versus σ_2 for plane strain deformation under triaxial stress. A least squares fit of a straight line to the data is shown.

The plane stress section of the engineering yield stress locus follows the pressure modified von Mises criterion with values of μ = 0.14 and 0.09 for rapidly cooled and annealed polycarbonate respectively. The errors in these values are estimated to be ± 0.02. The effect of annealing for 4 hours at 135°C is to increase the dimensions of the plane stress section by 15%. In a recent discussion of the difference between the uniaxial compression and tension yield stresses (10), the yield criterion of eq. (1) was assumed to apply and a value μ = 0.19 deduced from the measured engineering stresses. However estimating the true yield stresses reduced this value to 0.075. We have estimated the result for true stresses as follows: the engineering strain at yield in uniaxial compression was −0.08 whereas the reported volume change (11) was −1.1%; similar figures for uniaxial tension (12) were 0.035 and + 0.5%. As a result the compression to tension true stress ratio is 0.90 of the engineering stress ratio, and the estimated μ values for a true plane stress locus are 0.07 and 0.02. Thus the result from the plane true stress locus is in agreement with that from tensile tests under hydrostatic stress with a value of μ = 0.05 ± 0.03.

Since completing this investigation there has been a report (13) of tension and compression testing of thin walled polycarbonate tubes with internal pressurization. These authors found that the true 0.3% offset yield stress (this is really the onset of anelastic behavior not permanent plastic deformation) fitted either eq. (2) with $\mu = 0.13$ or a yield criterion of the form $J_2 + ap = K^2$ where a is a constant.

Conclusions

It has been shown that the plane stress section of the yield locus of polycarbonate can be described by Drucker's modification of the von Mises yield criterion rather than a complex hyprotrochoidal criterion. The value of the pressure dependence parameter μ agrees with data from the pressure dependence of the tensile yield stress if true stresses are considered.

M. J. Miles is grateful for the support of a Science Research Council Studentship.

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Received May 1, 1973
Revised July 16, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 569–572 (1973)

CARBON-13 NMR OF UV-ISOMERIZED POLYBUTADIENE STUDY OF ^{13}C-NMR SIGNAL DUE TO CIS-TRANS LINKAGE

Recently Mochel (1) investigated the ^{13}C-NMR spectra of polybutadienes and the model compounds such as cis, trans, trans-1,5,9-cyclododecatriene, 3,7-decadiene and cis, trans-4,8-dodecadiene and concluded that there are no cis-trans linkages in an n-BuLi-catalyzed polybutadiene. The conclusion was based on the finding that the model compounds showed the signals due to the methylene carbons of cis-trans linkage besides those of cis-cis and trans-trans linkages, while there apparently were no signals corresponding to the cis-trans linkage in the spectrum of the polybutadiene. However, this evidence seems not to be conclusive, since the polymer and its model compounds of low molecular weight have not always the same spectral features.

In this work we studied the ^{13}C-NMR spectra of cis-trans isomerized polybutadienes, in which the cis-1,4 and the trans-1,4 units are distributed randomly along the chain, and found that the signals due to the cis-trans linkage does not appear in spite of the existence of the cis-trans linkage in the polymer chain.

Isomerization of polybutadiene was carried out in benzene (2% solution) at room temperature with high-pressure mercury lamp by the use of diphenyl disulfide as an initiator (2). ^{13}C-NMR spectra were measured in dioxane (13 w/v%) with a JEOL JNM-PS/PFT-100 spectrometer at 25.15 MHz. Chemical shifts were referred to tetramethylsilane as an external standard. All the spectra were proton noise decoupled and were multiple scans.

In Figure 1 are shown the ^{13}C-NMR spectra of three samples of ultraviolet-isomerized polybutadienes. The samples A and B were obtained from cis-1,4-polybutadiene and the sample C from trans-1,4-polybutadiene. All the spectra showed two peaks at 28.4 and 33.6 ppm in methylene carbon region, which were assigned by Mochel (1) and Alaki et al. (3) to the methylene carbons of cis-cis and trans-trans linkages respectively. No other peaks were observed in this region except for the very small ones in the spectrum of C at 30.9, 35.0 and 39.1 ppm being assigned to the carbons of 1,2-1,4 linkage (3). The microstructures of the polymers determined from the intensity measurements of the methylene carbon signals were in good agreement with those by infrared spectroscopic method according to Morero et al. (4) as shown in Table I.

Olefinic carbons of all the polymers showed two peaks at 130.4 and 131.1 ppm, which were also assigned to cis-cis and trans-trans linkages (3).

Berger and Buckley (5) investigated the melting behavior and the X-ray diffraction pattern of the ultraviolet-isomerized polybutadiene and concluded that the distribution of cis and trans units along the polymer chain is statistically random regardless of the isomerization being started from trans-1,4 or cis-1,4-polybutadiene.

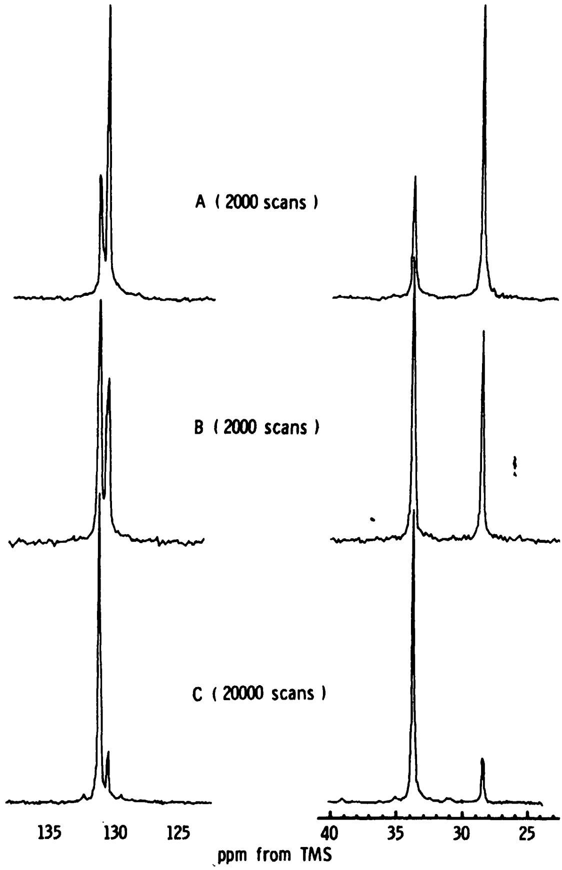

Fig. 1. Carbon-13 Fourier transform NMR spectra of ultraviolet-isomerized polybutadienes.

TABLE I

Microstructure of Ultraviolet-Isomerized Polybutadiene

Sample		cis-1,4	trans-1,4	1,2
A	IR	72.4	25.1	2.5
	NMR	73.6	26.4	–
B	IR	38.4	58.3	3.3
	NMR	42.2	57.8	–
C	IR	13.2	81.7	5.1
	NMR	12.0	83.8	4.2

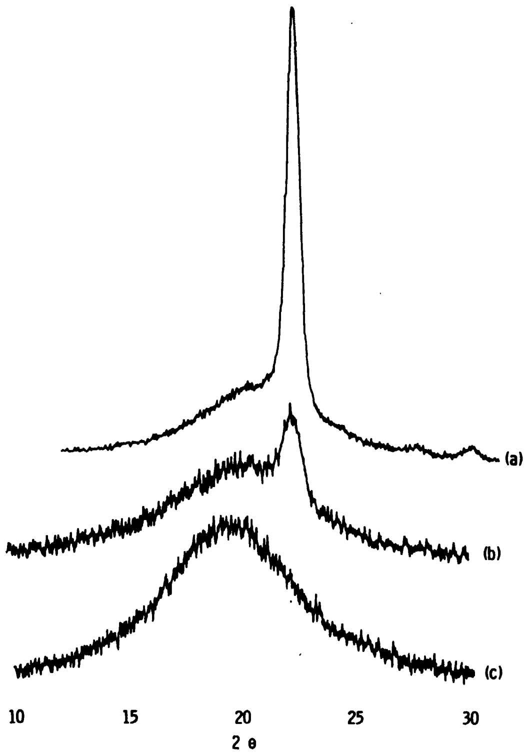

Fig. 2. X-ray diffraction patterns of (a) trans-1,4-polybutadiene, (b) the polybutadiene isomerized therefrom (C in Table I), and (c) the isomerized polybutadiene from cis-1,4-polymer (B in Table I).

The evidence for the random isomerization was also obtained by the X-ray analyses of trans-1,4-polybutadiene and the isomerized polybutadienes. The high crystallinity of trans-1,4-polybutadiene greatly decreased through the isomerization reaction as shown in Figures 2a and 2b. Moreover, the crystallinity due to the successive sequence of trans-1,4 unit did not appear during the isomerization of cis-1,4-polybutadiene even in the isomerized polymer having 58.3% of trans-1,4 unit (Fig. 2C). On the other hand, it has been shown that the ultraviolet isomerization reaction has not resulted in the molecular weight breakdown (5). This excludes the possibility that the isomerization breaks the chain into small enough segments such that the x-ray pattern becomes more amorphous. These facts indicate the random distribution of trans-1,4 unit in the isomerized polymer chain.

It was found that in the ^{1}H-NMR spectra of the isomerized polybutadienes the methylene proton signals decoupled from the olefinic protons split into three peaks which correspond to the methylene protons of cis-cis, cis-trans and trans-trans linkages (6). This is another support for the random distribution of cis-1,4 and trans-1,4 units in the polymer chain.

On the basis of the facts mentioned above, it is concluded that the methylene carbon in the cis-1,4 unit of the cis-trans linkage resonates at the same magnetic field as that of the cis-cis linkage, and in a similar way the trans-1,4 methylene carbons of the cis-trans linkage and of the trans-trans linkage resonate at the same position. The difference between the spectral features of the model compounds used by Mochel (1) and the isomerized polybutadienes might be attributed to the conformational difference around the methylene carbons in the solution.

The authors are very grateful to Drs. M. Imanari and K. Matsushita of JEOL Co., for the measurements of ^{13}C-NMR spectra, and to Mr. M. Ikeyama of Japan Synthetic Rubber Co., for his help in the laboratory work. They also express their hearty thanks to Mrs. F. Yano for her clerical assistance in preparing manuscript.

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Received June 6, 1973
Revised July 19, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 573–581 (1973)

RANDOM COPOLYMERIZATION OF ACETYLENE AND BUTADIENE

It is well known that the copolymerization of acetylene compound and conjugated diolefin is difficult owing to the much difference between their polymerization reactivities as well as their coordination ability to the catalyst. For instance, acetylene and butadiene were copolymerized to give a block copolymer (1), or cotrimerized to give a cyclotriene (2).

The present authors succeeded in the copolymerization of acetylene and butadiene to give a random copolymer. This report deals with the preparative method of the copolymer and its structure.

Experimental

The polymerization was performed under oxygen-free dry nitrogen atmosphere. Nickel naphthenate and solvent toluene were placed in a glass flask, and diethyl aluminum chloride (2 mole/liter hexane solution) was added. The catalyst mixture was allowed to react for 10–20 min at 20–30°C under agitation prior to the monomer charge. At 20°C, the mixed gas of acetylene and butadiene (23/77 in molar ratio) was bubbled into the catalyst solution at a flow rate of about 4.2 liter/hr. Bubbling and agitation were continued for 3 hr. The reaction mixture was poured into a large amount of methanol containing a small amount of 2,6-di-tert-butyl-p-cresol as a stabilizer. The liquid polymer was isolated in the lower layer. The liquid polymer recovered was dissolved in chloroform and the soluble polymer was separated from the insoluble part by the filtration. The solvent was then evaporated and the yellow viscous liquid or waxy polymer was obtained.

The microstructure of the polymer was determined by the IR method (3). The polymer composition and its sequence distribution were evaluated by 60 MHz NMR spectra measured with a polymer solution of ca. 10% (weight/volume) concentration in deuterochloroform at room temperature with tetramethylsilane as an internal standard. The intrinsic viscosity number was measured in toluene at 30 ± 0.05°C with an Ubbelohde type viscometer.

Results and Discussion

As a result of various kinds of screening experiments, it was found that dialkylaluminum halide with nickel carboxylate or nickel complex polymerizes butadiene and acetylene to give random and linear copolymers. The typical examples of polymerization results are summarized in Table I. The copolymer composition and the catalyst activity for the polymerization were influenced delicately by the preparation conditions of catalyst. Probably, the active

TABLE I

Copolymerization of Acetylene and Butadiene

Exp. No.	Catalyst reaction: Temp. (°C)	Catalyst reaction: Time (min)	Polymer: Yield (g)	CHCl$_3$ soluble polymer: (g)	CHCl$_3$ soluble polymer: A[a]	Microstructure (%): cis	Microstructure (%): trans	Microstructure (%): vinyl	[η]
604	20	10	3.01	1.63	0.441	81.0	11.1	7.9	–
631	25	10	11.98	8.37	0.296	83.7	10.0	6.3	0.12
659	30	10	17.61	14.71	0.180	83.6	11.1	5.3	–
661	30	20	7.35	4.86	0.382	82.2	9.9	7.9	–
625[b]	20	10	9.44	6.97	0.323	82.5	11.1	6.4	0.13

Polymerization conditions: Diethylaluminum chloride, 15 mmole; nickel naphthenate, 3 mmole; toluene, 70 ml; monomer feed rate, 4.2 liter/hr; acetylene/butadiene, 23/77 (molar ratio); polymer temp., 20°C; time, 3 hr.

[a]Molar fraction of acetylene in the copolymer

[b]Catalyst was prepared in the presence of acetylene.

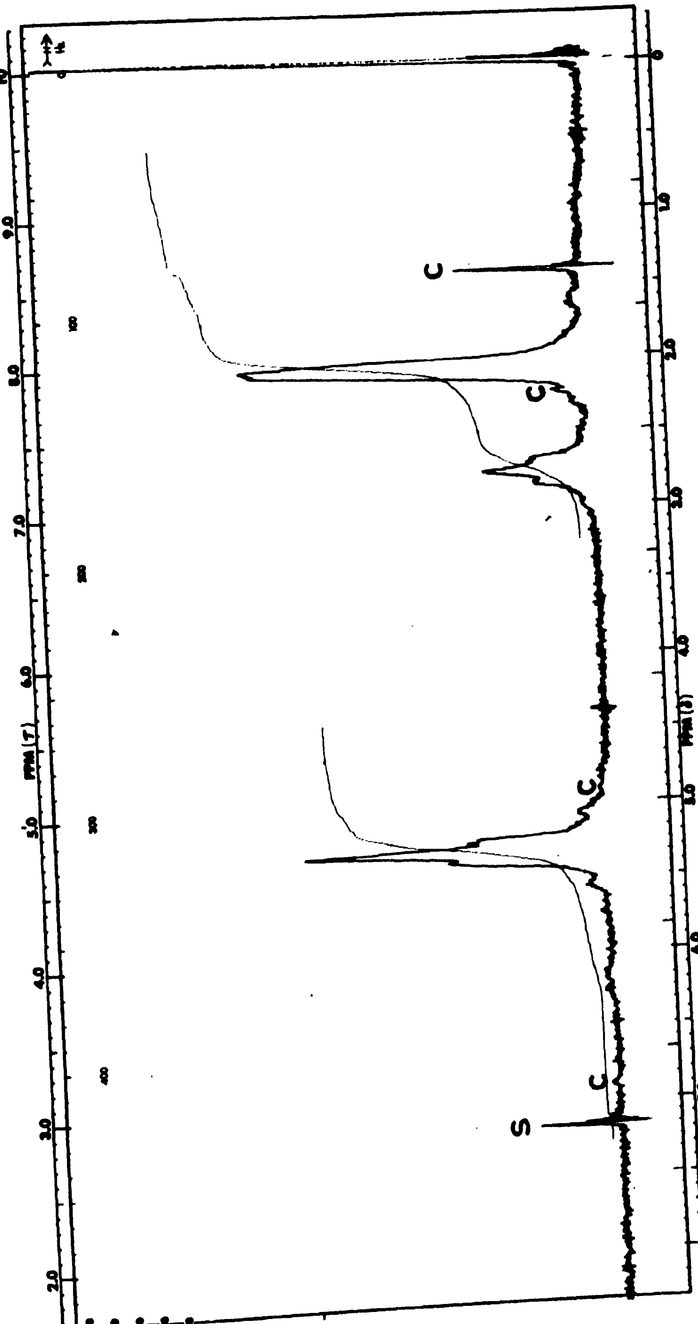

Figure 1a

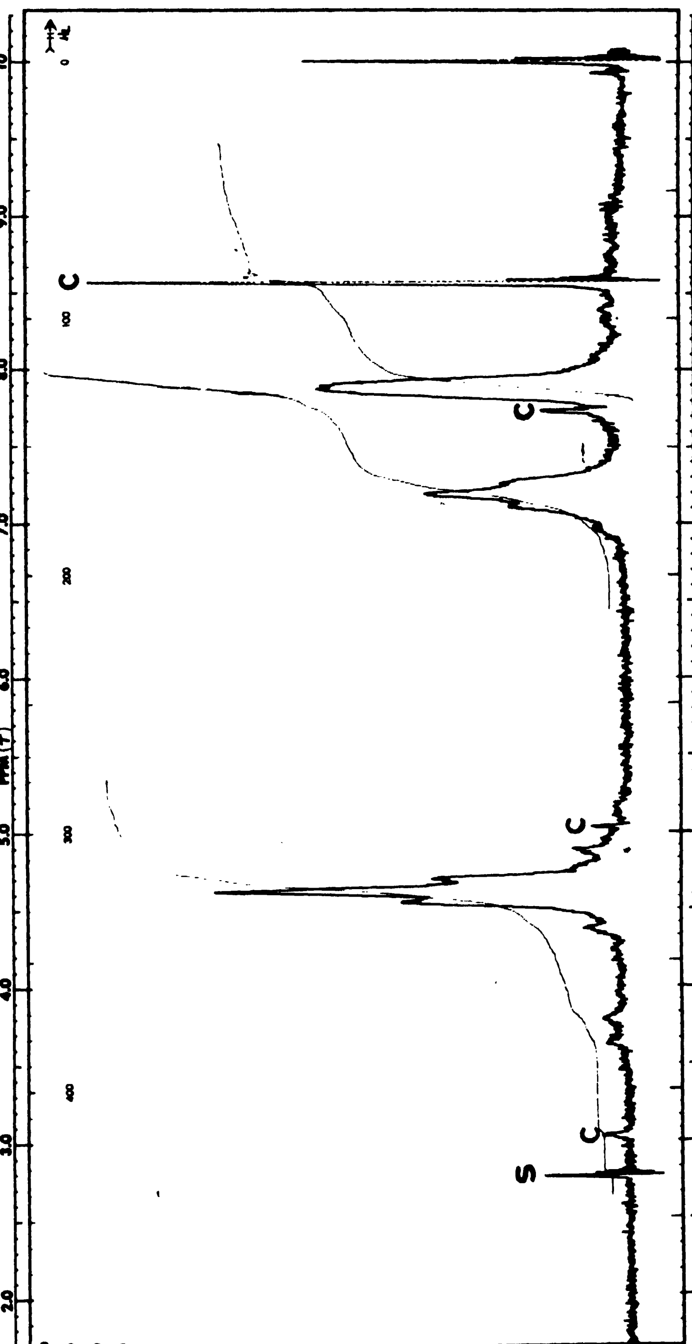

Figure 1b

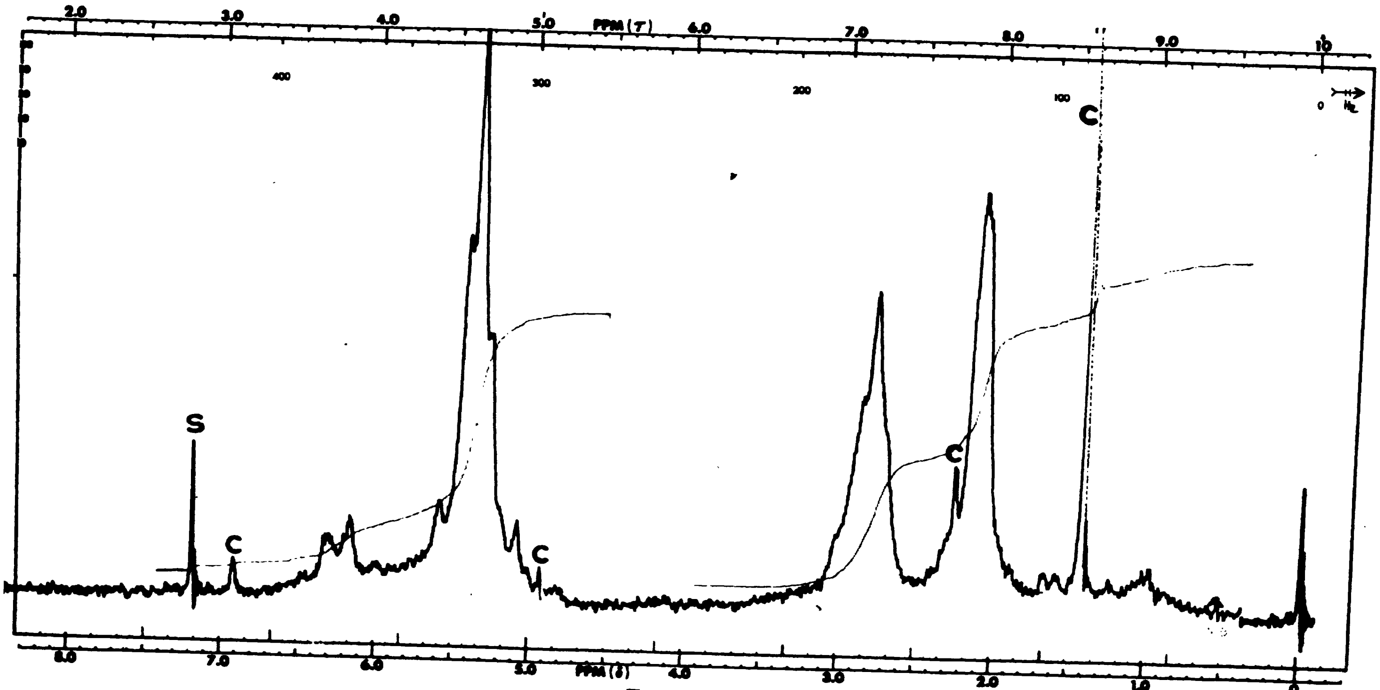

Figure 1c

Fig. 1. NMR spectra of copolymers of acetylene and butadiene: s is the impurity in the solvent; c is di-tert-butyl-p-cresole.

	a	b	c
Exp no.	631	661	604
Acetylene content (molar fraction)	0.296	0.382	0.441

species for the copolymerization may be formed by the complex formation between aluminum compound and nickel compound.

Figure 1 shows 60 MHz NMR spectra of copolymers containing various amount of acetylene unit. There are five peaks due to the solvent impurity (7.22 δ) and the stabilizer (1.43, 2.28, 4.97, and 6.98 δ). The peaks at 4.80–5.01 δ are scarcely observed, and therefore, vinyl unit of butadiene is negligible. This is compatible with the data determined by the IR method. The microstructure of the copolymers is mainly composed of the cis-1,4 unit and the vinyl unit is only 5–8% as shown in Table I. The assignments of the NMR spectra are attempted on the basis of the correlation with those of polybutadiene and of the model compounds. The peak at 2.12 δ is assigned to methylene protons of butadiene unit belonging to the butadiene–butadiene dyad. The value is found to be close to the chemical shift for the cis-1,4-polybutadiene (2.12 δ).

$$\vdots\,\mathrm{CH_2-CH{=}CH-C\underline{H}_2}\,\vdots\,\mathrm{C\underline{H}_2-CH{=}CH-CH_2}\,\vdots$$

The peak intensity at 2.82 δ increases with increasing the amount of acetylene content in the copolymers. It is likely that the peak is closely related to the acetylene–butadiene sequences, i.e., methylene protons of butadiene unit adjecent to acetylene unit.

$$\vdots\,\mathrm{CH{=}CH}\,\vdots\,\mathrm{C\underline{H}_2-CH{=}CH-CH_2}\,\vdots$$

In the case of linoleic acid, linolenic acid and methyl linolenate, the peaks of diallyl type protons are also observed at 2.77, 2.78 and 2.80 δ (4), respectively. These spectral behaviours are compatible with that of acetylene–butadiene copolymers.

The peak at 5.40 δ is assigned to methyne protons of butadiene unit and those of acetylene unit isolated by butadiene units,

$$\vdots\,\mathrm{CH_2-C\underline{H}{=}C\underline{H}-CH_2}\,\vdots$$

and

$$\vdots\,\mathrm{CH_2-CH{=}CH-CH_2}\,\vdots\,\mathrm{C\underline{H}{=}C\underline{H}}\,\vdots\,\mathrm{CH_2-CH{=}CH-CH_2}\,\vdots$$

The peaks at 6.22–6.37 δ are assigned to methyne protons of acetylene unit of the acetylene–acetylene dyad.

$$\vdots\,\mathrm{CH_2-CH{=}CH-CH_2}\,\vdots\,\mathrm{C}\underset{a}{\underline{\mathrm{H}}}{=}\mathrm{C}\underset{b}{\underline{\mathrm{H}}}\,\vdots\,\mathrm{C}\underset{b}{\underline{\mathrm{H}}}{=}\mathrm{C}\underset{a}{\underline{\mathrm{H}}}\,\vdots\,\mathrm{CH_2-CH{=}CH-CH_2}\,\vdots$$

H_a and H_b may be 6.22 and 6.37 δ, respectively.

A peak cannot be observed at lower field than 6.37 δ, and therefore long

polyacetylene sequence (longer than triad) are substantially absent in the copolymers.

The copolymer composition is evaluated as follows. Here, A denotes the molar fraction of acetylene in the copolymer, and R denotes the ratios of areas at 2.12 δ + 2.82 δ and 5.40 δ + 6.22–6.37 δ. Then, the following relation is derived.

$$R = \frac{4(1 - A)}{2A + 2(1 - A)},$$

and consequently,

$$A = 1 - \frac{R}{2}. \tag{1}$$

The dyad fraction is evaluated as follows. Here, F_{AA}, F_{AB} and F_{BB} denote the dyad fractions of acetylene–acetylene sequence, acetylene–butadiene sequence, and the butadiene–butadiene sequence, respectively. R′ denotes the ratios of areas at 2.82 and 2.12 δ. It follows that

$$\frac{F_{AB}}{F_{BB}} = \frac{(\text{area at } 2.82\ \delta)/2}{(\text{area at } 2.12\ \delta)/4} = 2\ R'$$

and consequently,

$$F_{AB} = 2\ R' \cdot F_{BB}. \tag{2}$$

Here, the molar fraction of butadiene unit in the copolymer B or 1-A is

$$B = F_{BB} + \frac{F_{AB}}{2} \tag{3}$$

From (2) and (3), F_{BB} is expressed as follows:

$$F_{BB} = \frac{B}{1 + R'} \tag{4}$$

From the relation,

$$F_{AA} = 1 - (F_{AB} + F_{BB}) \tag{5}$$

and equations (2), (4) and (5), the dyad fractions are evaluated.

If the copolymer is random with respect to the sequence distribution of acetylene and butadiene units, the dyad fractions are calculated as follows according to Bernoullian statistics (5).

TABLE II

Dyad Fractions

Exp. No.	A	Evaluated from NMR F_{AA}	Evaluated from NMR F_{AB}	Evaluated from NMR F_{BB}	Calculated from random assumption F_{AA}	Calculated from random assumption F_{AB}	Calculated from random assumption F_{BB}
659	0.180	0.035	0.290	0.675	0.032	0.295	0.673
631	0.296	0.111	0.370	0.519	0.088	0.417	0.495
625	0.323	0.128	0.391	0.481	0.104	0.437	0.459
661	0.382	0.115	0.537	0.348	0.146	0.472	0.382
604	0.441	0.189	0.505	0.306	0.195	0.493	0.312

TABLE III

Fractionation of the Copolymer (Exp. No. 625)

Polymer wt (%)	Original 100	Fractionated[a] Soluble 27	Fractionated[a] Insoluble 73
$[\eta]$[b]	0.128	0.086	0.167
A[c]	0.323	0.335	0.361

[a]6.64 g of copolymer was fractionated with $CHCl_3/CH_3OH$ (50/30 ml) at room temperature.

[b]Measured in toluene solution at 30 ± 0.05°C.

[c]Molar fraction of acetylene in the copolymer.

$$F_{AA} = A^2$$

$$F_{AB} = 2AB$$

$$F_{BB} = B^2$$

The dyad fractions evaluated from NMR and those calculated from random assumption are shown in Table II. Both values are relatively close. Therefore, the sequence distribution of these copolymers is to be mostly random.

The fractionation of the polymer keeps the copolymer composition almost constant irrespective of molecular weight ($[\eta]$) as shown in Table III. Thus, the copolymer is to be of homogeneous composition.

Considering the results of the NMR analysis and the fractionation, this polymer is not to be a blend but a copolymer. The details will be published later.

The authors wish to express their thanks to Miss H. Shimomi for her help in measuring NMR spectra.

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Received December 27, 1972
Revised June 5, 1973

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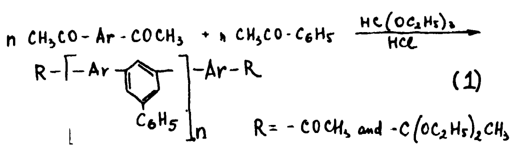
POLYMER LETTERS EDITION VOL. 11, PP. 583–587 (1973)

NEW METHOD FOR SYNTHESIS OF POLYMERS OF THE POLYPHENYLENE TYPE APPLYING POLYCYCLOCONDENSATION OF DIACETYLAROMATIC COMPOUNDS

Synthesis and investigation of the thermally stable polymers are at present one of the main directions in high polymer chemistry. The polymers, consisting of alternating benzene nuclei, polyphenylenes, are one of the most promising classes of thermally stable polymers (1). In modern practice, there are some ways for obtaining polyphenylenes which are adequately covered in literature reviews (2–4), but all these methods involve one or another disadvantages, as for instance, complicated synthesis of initial compounds, difficulties in polymer processing, and so on. A very actual problem is the search for new synthesis methods of polyphenylenes promising mainly from the technological point of view.

In this study, we have investigated the possibility of using the known reaction of methylketone condensation yielding 1,3,5-substituted benzene cycles (5–7) to synthesize polyphenylenes by polycyclocondensation of diacetylaromatic compounds (8).

p-Diacetylbenzene, 4,4′-diacetyldiphenyl, and 4,4′-diacetyldiphenyloxide have been used as initial diacetyl compounds. Using only diacetyl compounds results in the formation of infusible and insoluble three-dimensional polyphenylenes in a very short time. The mixture of a diacetyl compound with a monoacetyl compound, for instance, acetophenone, yields less branched polymers. For equimolar ratio of those and similar reactivities, linear polymers are assumed to form according to the following scheme:



(1)

Nevertheless, even with the monoacetyl monomer the polymer was found to precipitate from solution at some instant probably due to gelation on monoacetyl consumption or to decreasing solubility of the system. Thus, the polycyclocondensation reaction was completed at the stage of soluble polyphenylenes and those were then converted to the resulting products on heating.

The polycondensation reaction was carried out at room temperature in an inert solvent, usually dry benzene, in the presence of ethyl ortho-formate (1.2 mole per acetyl group of the initial mixture), which considerably accelerates the polymer synthesis. The polymer was precipitated with ethyl alcohol and washed with soda solution and water to remove the HCl traces completely.

TABLE I

Properties of Oligomeric Polyphenylenes

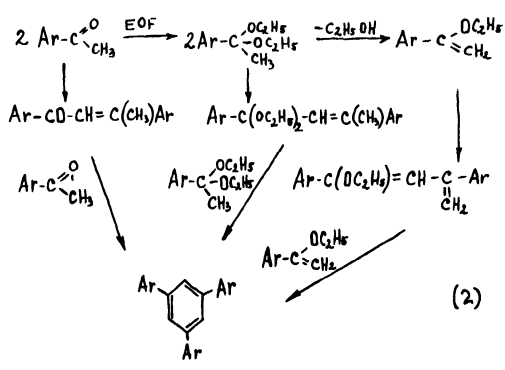
No.	Initial diacetyl	Mole amount of acetophenone per 1 mole of diacetyl	Synthesis conditions: Time, min	Synthesis conditions: Temperature, °C	Solubility[a]: Reaction solution	Solubility[a]: Benzene	Solubility[a]: Chloroform	Found, %: C	Found, %: H	Mol. wt. (ebullioscopic in chloroform)
1	p-Diacetylbenzene	0	20	~20	-	-	-	85.4	5.3	crosslinked polymer
2	p-Diacetylbenzene	0	10	20	+	+	+	84.2	5.4	1600
3	p-Diacetylbenzene	0.8	15	20	+	+	+	88.7	5.8	3500
4	p-Diacetylbenzene	1.0	15	20	+	x	+	89.9	5.4	3100
5	p-Diacetylbenzene	1.0	60	15	+	-	x	89.7	5.0	>4100[c]
6	p-Diacetylbenzene	1.6	15	~20	+	+	+	88.2	5.6	1200
7	p-Diacetylbenzene	2.4	15	~20	+	+	+	87.9	5.3	760
8	[a]4,4'-Diacetyldiphenyloxide	0.8	20	15	+	x	+	88.2	5.2	2200
9	[b]4,4'-Diacetyldiphenyloxide	1.2	60	~20	+	x	+	86.0	4.6	4200
10	4,4'-Diacetyldiphenyloxide	1.6	600	15	+	+	+	85.0	5.1	1540
11	4,4'-Diacetyldiphenyl	1.6	60	0	+(40%)	x	+	89.6	5.6	1280
					-(60%)	-	-	88.4	5.6	crosslinked polymer

[a] + soluble; x partially soluble; - insoluble.

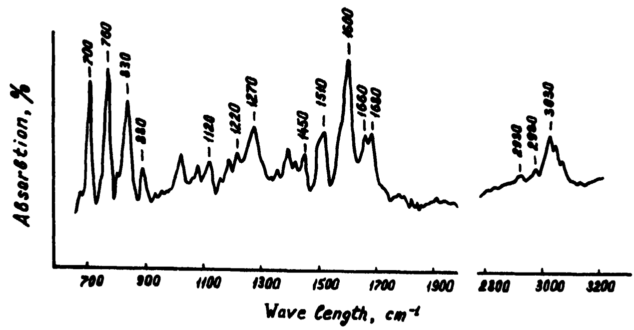
[b] Samples extracted with ethanol.

[c] Reduced viscosity of the fraction soluble in $CHCl_3$ is 0.22 dl/g (that of a similar polymer of mol. wt. of 4100 was 0.18 dl/g).

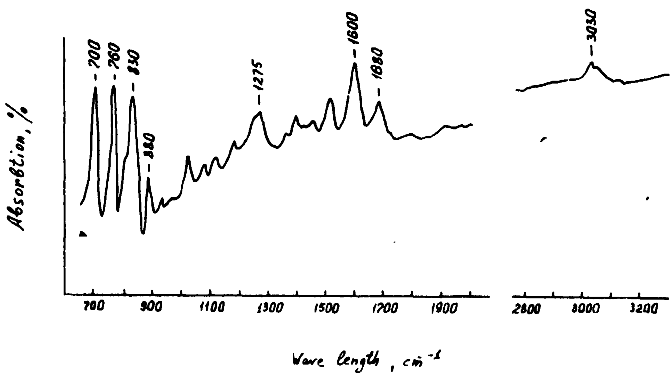
As a whole, the polycyclocondensation reaction is a rather complex process, and its rate depends substantially on a number of factors. This is first of all due to the complexity of the very formation of the benzene ring, where on crotonic condensation of the acetyl groups first dimer (dipnone–$P_hCOCH{=}C(CH_3)P_h$) or dipnone fragments and then a trimer is formed, intramolecular cyclization of the latter giving a 1,3,5-substituted benzene ring (9). Ethyl-orthoformate (EOF) accelerates the reaction not only as a dehydrating agent. In an acidic medium, EOF can easily change the acetyl compounds to ketals (7), which can be converted to vinyl ethers (10). It is known (7,11) that these groups can easily be trimerized to form a benzene ring. Moreover, it is common knowledge that the use of ketals also gives rise to polyphenylene synthesis (12). Thus, the mechanism of elementary act of polyphenylene formation by polycyclocondensation in the presence of EOF and HCl can be described by the following scheme:



(2)



1a



1b

Fig. 1. a. Infrared spectra of polymer No. 5 (Table I).
b. Infrared spectra of the cured polymer No. 5 at 300°C.

The basic data on polyphenylene synthesis in solution are given in Table I. The formation of polyphenylenes was confirmed by the infrared spectra (13) and primarily by the appearance of a 880 cm^{-1} absorption band characteristic of out-of-plane deformation vibrations of the isolated hydrogen atom of the 1,3,5-substituted benzene ring. The presence of ketal and acetyl groups in polymers is confirmed by the bands at 1680 and 1275 cm^{-1} characteristic of the C=O stretching of aromatic ketones, as well as by the bands at 1060, 1100-1130, and 1150-1175 cm^{-1} characteristic of the aliphatic C—O bond. This is examplified by Fig. 1a showing the spectrum of polyphenylene based on p-diacetylbenzene (polymer No. 5, Table I). The band at 880 cm^{-1} is assigned to the 1,3,5-substituted benzene ring, and the bands at 700 and 760 cm^{-1} are characteristic of the phenyl substituent. An intense band at 830 cm^{-1} is attributed to the 1,4-substituted benzene ring, and the bands at 1080, 1120, and 1180 cm^{-1} arise, as mentioned above, from the endgroups. The endgroups are responsible for a combined absorption band of C—H deforma-

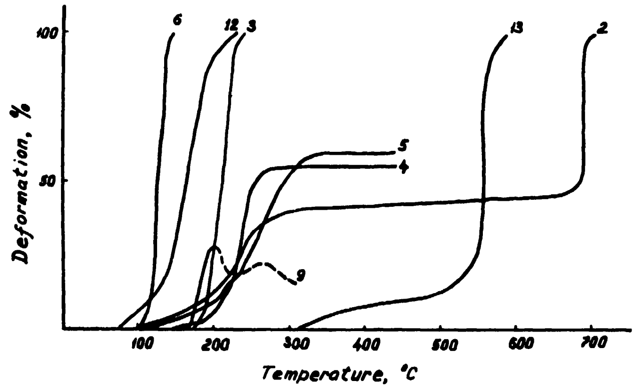


Fig. 2. Thermomechanical curves. Order numbers of the curves correspond to those of polymers of Table I. No. 12 is obtained as polymer No. 3 at a monomer ratio of 1:1.3. No. 13 is polymer No. 5 heated at 300°C.

tion vibrations of the methyl and methylene groups at 1450 cm^{-1} and of a weak intensity band of C—H stretching at 2930 and 2980 cm^{-1}. The 1670 cm^{-1} should be considered to correspond to a carbonyl group of the dipnone unit in polymer, if it is remembered that there is a band corresponding to this group also at 1200 cm^{-1}. Intense bands at 1510, 1600, and a moderately intense band at 3030 cm^{-1} are attributed to C=C and C—H vibrations of the benzene ring.

The elementary analysis (Table I) of the resulting polyphenylenes gives only relative data, since the structure of polymeric chain and endgroups, as well as the amount of "defective structures" are obscure. But if the polyphenylenes obtained with equimolar ratio of di- and monoacetyls are assumed to have two ketal endgroups, all the data are in satisfactory agreement,* which points to a relatively low content of defective dipnone units.†

An analysis of basic properties of polyphenylenes obtained from various initial compounds and with various ratio of di- and monoacetyl monomers shows (Table I and Fig. 2) that in all cases there is a common tendency of the influence of the ratio of di- and monofunctional monomers. The optimum is an equimolar ratio or one close to it. The increase in a part of monoacetyl decreases the molecular weight due to chain termination. In the case of 4,4′-diacetyldiphenyl, there is probably a significant difference in monomer reactivities, which is confirmed by the presence of an insoluble polymer fraction even at a ratio 1:1.6. As seen from thermomechanical curves (Fig. 2), the polyphenylene properties obtained at the first stage depend not only on the

*Calculated for oligomer No. 4 (Table I): C 89.2; H 5.6%.

†It should be considered that an incomplete combustion of polyphenylenes found recently for poly-p-phenylene[14] can result in the underestimation of data for C.

structure of the initial components and their ratio, but also on synthesis conditions, which mostly determine the molecular weight and the endgroup content of these polymers.

The soluble polyphenylenes formed at the first stage of a rather low molecular weight can be converted to three-dimensional polymers of a polyphenylene type on heating at 300°C in an inert atmosphere by subsequent endgroup condensation.

There are, however, some residual endgroups in the polymer chain of the cured polymer. This was confirmed by the presence in infrared-spectra of the band at 1680 cm^{-1} characteristic for C=O group (Fig. 1b) and by the odds between the elementary analysis data for the cured polymer (C = 91.5%; H = 5.1%) and for polyphenylene unit (C = 94.7%; H = 5.3%).

A two-stage process enables one to obtain at the second stage ready-made articles from polymers, which possess high thermal and heat stability. Easy of fabrication along with availability of initial monomers make this method rather promising for obtaining practically useful polymeric materials.*

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Received February 15, 1973
Revised July 13, 1973

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POLYMER LETTERS EDITION VOL. 11, PP. 589–593 (1973)

NEW METHOD OF SYNTHESIS OF POLYPHENYLENE TYPE POLYMERS USING POLYCYCLOCONDENSATION OF KETALS

Within the last few years the polycyclotrimerization of various monomers has been successfully used in polyphenylene synthesis (1–4).

To synthesize polyphenylenes, the cyclotrimerization of ketals of methylarylketones was carried out in the presence of acidic catalysts to form a 1,3,5-substituted benzene cycle (5). In order to prepare polymers suitable for processing of ready-made articles, the synthesis was performed in two stages: at the first stage fusible and soluble products with reactive endgroups were obtained, and at the second stage the synthesized polyphenylenes were converted to network polymers by heating (6,7).

The data obtained on the investigation of a model reaction of cyclotrimerization of ketal of acetophenone (8) were taken into consideration in a study on basic regularities of copolycyclocondensation of ketals of mono- and diacetyl compounds to form polyphenylene type polymers.

On examining the polycyclocondensation of difunctional diethylketal of p-diacetylbenzene, one can arrive at the conclusion that already in the first reaction step giving 1,3,5-substituted benzene cycles the branching of the polymer begins, which subsequently must lead to the formation of a network structure. It is quite clear that this process will be considerably affected by the catalyst concentration. As can be seen from the data of Figure 1, the synthesis dura-

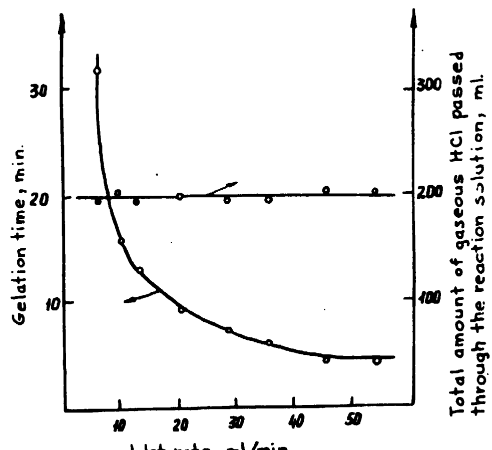


Fig. 1. Dependence of the gelation time and catalyst consumption on its inlet rate.

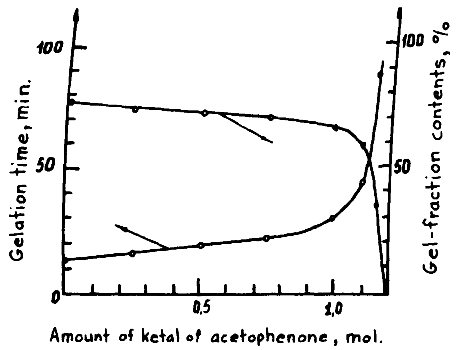
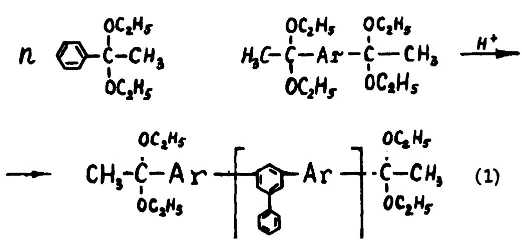


Fig. 2. Influence of the amount of ketal of acetophenone on the gelation time and the gel-fraction contents in copolycyclocondensation with ketal of p-diacetylbenzene.

tion to gelation point decreases as the HCl inlet increases, the total catalyst consumtion being constant. Thus, the process rate can be controlled by dosing out the catalyst amount.

The branching reaction of the polymer can be decreased by blocking a definite portion of functional groups. Blocking can be achieved by means of copolycyclocondensation of ketals of mono- and diacetyl compounds. The data of Figure 2 show that the increase in the ratio of monofunctional compound to bifunctional gives rise to the decrease of the gelation rate and the increase of the portion of soluble fraction. With the molar ratio of 1.2, there is no gel formation for 2.5 hr. The increase in the blocking agent amount, however, decreases the molecular weight of soluble polymer and the functional end-groups, which is undesirable for the reaction of polymer curing. Assuming that the activity of the ketals of mono- and diacetyl compound during polycyclocondensation would be very close and in addition by-processes would be absent, a linear polyphenylene can be obtained with the equimolecular component ratio. All further syntheses were carried out with the equimolecular ratio of starting ketals. This reaction can be schematized as follows:


(1)

In polyphenylene synthesis, ethyl ketals of p- and m-diacetylbenzene, 4,4'-diacetyldiphenyl, 4,4'-diacetyldiphenyloxide, and 4,4'-diacetyldiphenylmethane

TABLE I

Properties of Polyphenylenes Based on Ethyl Ketals of Diacetylarylenes and Acetophenone at a Mole Ratio of the Starting Substances of 1:1

No.	Starting diacetyl compound	Element composition				Mol. wt ebulliosccopic in chloroform	Flow temperature, °C[b]	End group content from NMR data
		Calcd., %[a]		Found, %				
		C	H	C	H			
1.	p-$CH_3COC_6H_4COCH_3$	91.27	5.65	91.12	5.54	1800	150–170	1.9
2.	$CH_3COC_6H_4C_6H_4COCH_3$	91.22	5.72	90.56	5.55	1400	170–180	2.1
3.	$CH_3COC_6H_4CH_2C_6H_4COCH_3$	92.83	6.34	92.33	6.08	2900	100–110	1.8
4.	$CH_3COC_6H_4OC_6H_4COCH_3$	86.05	5.58	85.52	5.18	1860	100–120	1.9
5.	m-$CH_3COC_6H_4COCH_3$	91.27	5.65	90.10	5.62	4500	150-160	1.9

[a] Calculated for an polymer with two ketal endgroups

[b] Determined by the method described in ref.10 at a specific load of 100 kg/cm².

were used as starting compounds. The reaction was carried out in dry benzene solution at 20°C with HCl as catalyst and at an initial concentration of monomer solution of 1 g mole/liter. The properties of the polyphenylenes synthesized are given in Table I. The infrared spectrum of the products contains an absorption band at 880 cm^{-1} characteristic of the 1,3,5-substituted benzene cycle (9) and absorption bands at 1030, 1070, and 1120 cm^{-1} attributed to the vibration of the ketal endgroup bonds. The 1680 cm^{-1} band points to the partial hydrolysis of the ketal groups during catalyst washing.

The endgroup amount in the polyphenylene is approximately 2, as determined from the NMR-spectra data, which is indicative of its linear structure. NMR spectra were obtained on the Perkin-Elmer R-12″ apparatus for 15% solutions of the polymer in methylene chloride with hexamethyldisoloxane as standard. Integration of the benzene ring and CH_3 group from OC_2H_5 groups proton signals was accomplished in the range of 2.2–2.9 ppm (τ) and 8.6–8.9 ppm (τ), respectively.

The polyphenylenes synthesized were cured in an inert atmosphere at 300°C with p-toluene sulphonic acid as catalyst. Infusible and insoluble dark brown polymers were obtained. In the infrared spectrum of the cured products there were no bands characteristic of the endgroups vibrations.

In the process of curing an increase in the contents of 1,3,5-substituted benzene rings occur (comparison in data of intensity of 880 cm^{-1} and 760 cm^{-1} bands).

The cured polyphenylenes are rather thermally stable products. According

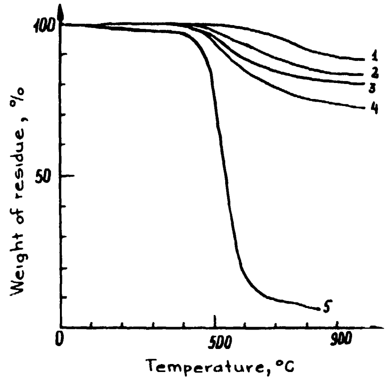


Fig. 3. DTA curves obtained in helium (1–4) and in air (5) at a temperature increase rate of 5°/min. 1–4 are polymers 1–4 of Table I. 5 is polymer 1 of Table I.

to TGA data, intense decomposition in helium begins at 480–520°C, and the weight loss on heating at 900°C does not exceed 10–15% (Fig. 3, curves 1–4). Intense decomposition of the cured polyphenylenes from ketal of p-diacetylbenzene in air takes place at about 450°C (curve 5). Somewhat lower initial decomposition temperature as compared to the known polyphenylene types can be explained by the presence of the residual endgroups and defective dipnone fragments.

Thus, the polycyclocondensation of ethyl ketals of diacetylarylenes enables one to synthesize the heat and thermally stable polyphenylene type polymers in a simple and convenient way.

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BOOK REVIEWS

Progress in Polymer Science Japan, Vol. 4, K. Imahori and Y. Iwakura, Eds., Halsted Press, New York, 1972. 278 pp. $14.00

This is the fourth volume of this series in which the first three chapters deal with the synthesis of polymers while the last two are concerned with the structure and properties of macromolecules.

In Chapter 1, "New Synthetic Routes to High Temperature Polymers by Cyclopolycondensation Reactions", N. Yoda, M. Kurihara, and N. Dokoshi, Toray Industries, provide an account of their work in "cyclopolycondensation reactions" involving the use of polyphosphoric acid as a reaction medium. This is a somewhat more up to date version of their review article (see J. Polymer Sci., D, 5, 109 (1971)) but has been narrowed primarily to a discussion of their own work. The mechanism(s) of the condensation reactions is still open to question, in my opinion, since the evidence for a mixed a hydride of the phosphoric and carboxylic moieties (infrared and nuclear magnetic resonance), and for the presence of high concentrations of free (unprotonated) amine (nuclear magnetic resonance), is not compelling; quantitative information is lacking and the isolation of intermediate model compounds has not been accomplished. Unfortunately, more information on the establishment of polymer structure and the properties of the polymers is not provided. The terms "good thermostability" and "better thermostability than" are used throughout, in many cases without quantitative data. Some TGA's curves are shown, but data on isothermal aging is not. For example, elaboration of the statement (p. 11) that a polyindolone with "excellent thermostability . . . was found to exhibit semiconducting properties" would have been an interesting and useful addition. In spite of these and several other minor difficulties with the chapter, it is very readable and provides a good source of references in the area.

Y. Iwakura, F. Toda, and Y. Torii, University of Tokyo, in Chapter 2, give a short summary of the reactions and polymer syntheses involving pseudoxazolones, which are relatively new to macromolecular syntheses. In many cases the polymers obtained are not high molecular weight, particularly in the ring opening reactions involving amines and mercaptans as well as the copolymerizations with oxygen and the H-addition polymerizations via oxazoline intermediates. Surprisingly, neither comment concerning the low molecular weights nor explanations for these results are offered. The explanation of oxazolone stability (p. 76) is somewhat contradictory and not as straightforward as it could be, but most of the chapter is written in readable style.

The synthesis and reactions of polymers containing reactive functional groups is the subject of Chapter 3 by M. Okawara, T. Endo, and Y. Kurusu, Tokyo Institute of Technology. This chapter is quite disappointing in that it

is concerned mostly with polymer syntheses while quantitative studies and more definitive studies on the reactions of the polymers is lacking. Comparisons of the reactions of the functional groups on the polymers with the reactions of model compounds containing these groups are not presented. The advantages, expected or realized, of the polymers systems are almost completely overlooked. Unfortunately this chapter also presents difficult reading and has not been carefully edited.

In the fourth chapter, H. Kawai and coworkers of Kyoto University discuss domain formation in block and graft copolymers which show microphase separation. Emphasis is on the mechanism of formation of such domains, with the analysis largely in terms of micelles, a type of molecular organization long studied by colloid chemists. There are obviously dangers involved in pressing such an analogy too far, but apparently a number of interesting interpretations of experimental results have been obtained by this approach.

The last chapter, contributed by M. Hatano and T. Nozawa of Tohoku University, is entitled "Metalloenzyme Models–Structure and Catalytic Activity of Poly-α-amino Acid-Metal Complexes." This article consists of a detailed discussion of the properties of the poly-L-lysine-copper(II) complex, in particular its assymmetrically selective catalysis of chemical reactions. It is an interesting story and will surely prompt additional, similar studies in the fascinating and very important area of biopolymer chemistry.

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Received July 16, 1973

An Introduction to Macromolecules, Heidelberg Science Library, Vol. 17, Leo Mandelkern, Springer-Verlag New York, Inc., New York, 1972. 161 + x pp. $5.90

"The History of mankind has been divided into a number of eras on the basis of the material common to the age. Thus we have passed through the stone, copper, bronze, and iron ages. The modern epoch may very well be

looked back on by historians as the Age of Macromolecules." These words open the first chapter of "An Introduction to Macromolecules." They state the author's perspective and imply his rationale for writing this book. Polymeric substances are revolutionizing the material accouterments of human society, and the understanding of their properties is a key to the most fundamental questions of biology. Yet university students, whether in science or humanities, typically have little opportunity to learn about macromolecules except in advanced technical or graduate courses. Recognizing this incongruity, Professor Mandelkern has fashioned a nonmathematical treatment organized around molecular structural concepts applicable alike to synthetic and natural polymers.

The compact second chapter outlines these fundamental ideas, lists chemical structures of important synthetic polymers and biopolymers, contrasts addition and condensation polymerization, and concludes with a discussion of branching and crosslinking. The next chapter, on chain conformation, gives what is perhaps the best elementary presentation this reviewer has seen of the isomeric rotational-state principle, and then delineates the relation between the real polymer chain and the idealized random-flight model. The remainder of the chapter deals with the correlation between intramolecular hindrances to bond rotation and the stability of ordered structures—the planar zigzag and helical conformations—in bulk polymers. The basis for tacticity in vinyl polymers is explained clearly.

One chapter is devoted to "Rubbers and Glasses." This begins with a phenomenological account of rubber elasticity and then continues with a succinct description of the molecular basis of the phenomenon. This section is the least satisfying part of the book. The discussion—and especially the diagram on p. 53—implying an exact antithesis between the normal three-dimensional thermal expansion of any materials and the contraction of an elongated rubber strip on heating under constant load is at least misleading. In the ensuing section on glass formation and the glass transition temperature, a welcome emphasis is placed on the kinetic nature of the distinction between the glassy and rubbery states. The brief mention of plasticizers falls naturally into place at the end of this chapter.

Ideas introduced earlier in connection with chain conformations are utilized in a more detailed consideration of crystalline polymers. Representative unit-cell structures are described, and then the kinetic aspects of crystallization in high and low molecular weight materials are contrasted to show why imperfect crystallization is typical of long-chain molecules. There follows a good description of the celebrated folded-chain single-crystal structure. Some readers may take exception at this point to a discussion that hews to the author's own position on the nature of the fold surface of the crystal lamellae without conceding that there is an opposing point of view. The ubiquity of lamellar crystallization from solutions and from melts is properly emphasized, but it is regrettable that nothing is said about the important spherulitic morphology. A section on the melting behavior of polymer crystals focusses on correlations

with chain structure–branching, content and distribution of copolymer units, geometrical and stereo isomerism, heterogeneity in chain length–and touches on the relation of the melting point and glass transition temperature to uses of plastics and fibers.

This chapter continues with a concise treatment of polymer fibers, their production, molecular morphology, and characteristic physical properties. It concludes with a section on mechanochemistry, illustrating the large-scale reversible dimensional changes attainable in contractile systems and establishing their origin in thermodynamic phase transitions (melting) dependent on temperature or the chemical environment.

The final chapter is on biological macromolecules. It is by far the longest and probably the best, comprising a remarkable amount of information within its span of 54 pages. It begins by detailing the structures of the 20 biologically important amino acids and continues with the conformations of polypeptides: the planar character of the amide group, the detailed geometry of the alpha helix, the beta conformation, and the unique left-handed polyproline helix. These matters introduce a discussion of proteins–including amino acid composition and sequences; supermolecular fibrous morphology as exemplified by alpha keratin, silk fibroin, and collagen; the secondary and tertiary structure of globular proteins. In the last category, enzymes and respiratory proteins are discussed to demonstrate the intimate relation between structure and biological function. The nucleic acids are the final major topic. Base-pairing between the complementary strands in the Watson-Crick helix is presented as the basis for transcription of genetic information via DNA replication and synthesis of the various RNA's. An account of the genetic code and the machinery for ribosomal synthesis of proteins then brings the reader to the frontier of molecular biology.

The text concludes with an epilogue, "Macromolecules and Man," that enlarges upon the humanistic concerns of the opening. A short reading list and an index are appended.

All in all, this work is a splendidly concise and informative summary of the wide sweep of macromolecular science. Its manner is resolutely descriptive. Although the whole book contains but seven mathematical equations–having to do with the random-flight chain and force versus extension in an ideal rubber–this abnegation is accomplished virtually without compromising precision, or clarity, or even the level of sophistication. An issue is scarcely ever avoided by resort to an it-can-be-shown type of argument. Apart from a drawing mentioned above and an electron micrograph (p. 76) that will scarcely convey to the novice what it is said to show, the exposition is enhanced by a great number of well-chosen well-designed illustrations, including many chemical structures.

The typography and design of the book are excellent. Much care was obviously put into proofreading. This reviewer detected few lapses save one or two grammatical slips and the jarring statement that Bakelite polymer "is easily molded into a variety of objects."

Perhaps the book most nearly like this one (and from the same publisher) is another excellent paperback "Introduction to Polymer Science" by L. R. G. Treloar. Comparatively, Mandelkern's book is more concerned with chemistry and Treloar's with physics. Treloar's discussions of synthetic fibers, tensile properties, and strength of materials are fuller than Mandelkern's; and his treatment of rheology has no counterpart in Mandelkern's book. On the other hand, Treloar has nothing like Mandelkern's précis of molecular biology. Treloar's style is more literary than Mandelkern's—perhaps a reflection of cultural traditions on the two sides of the Atlantic—but Mandelkern is more consistently successful in making the descriptive treatment carry the full burden of elucidating difficult concepts.

Mandelkern's book bears less similarity to "Organic Polymers" by Alfrey and Gurnee. Although this too is an introductory survey covering much the same subject matter except for biological macromolecules, it is addressed to relatively advanced students in a course in materials engineering, and presupposes knowledge of college-level chemistry, physics, and mathematics.

In sum, Mandelkern's educational purpose is an important one and he has achieved it in exemplary fashion. The two major themes—the relation of molecular structure to physical and chemical properties, and the relation of polymer science to molecular biology—lend his presentation an impressive unity. Certainly, it is not too much to claim that an appreciation of these two leading ideas and a familiarity with some of the specific factual information in this book are indispensable to the intellectual formation of any student who aspires to even a minimal understanding of the role of science in our civilization.

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Received August 7, 1973

Macromolecular Microsymposia, VIII and IX, B. Sedláček, Ed., Butterworths, London, 1972. 281 pp. $24.60

For some years the International Union of Pure and Applied Chemistry, the Czechoslovak Academy of Sciences, and the Czechoslovak Chemical Society have been cosponsors of an annual series of "Microsymposia"—four-day international meetings in Prague, each devoted to a major research area in macromolecular science. Each meeting is organized about a series of invited lectures reviewing the current status of the field and serving to introduce discussion sessions and presentation of short communications. The present volume is a

collection of the main lectures given at the Eighth (Morphology of Polymers) and Ninth (Thermodynamics of Interactions in Polymer Solutions) Microsymposia held in August and September, 1971.

A collection of this sort is perhaps best summarized by simply listing the titles: "Influence of Crystallization Conditions on Single Crystal Formation" (Nakajima and Hamada); "Formation of Supermolecular Structures in Thin Polymer Layers" (Kryszewski); "Extended-chain Crystals of Linear High Polymers" (Wunderlich); "Morphology of Amorphous Polymers and Effects of Thermal and Mechanical Treatments on the Morphology" (Yeh); "The Influence of Morphology on the Mechanical Properties of Crystalline Polymers" (Andrews); and "Effect of Annealing and Temperature on the Morphological Structure of Polymers" (Fischer).

"Role of Free Volume in Polymer Solution Thermodynamics" (Patterson); "Thermodynamic Interactions in Dilute Polymer Solutions: the Virial Coefficients" (Casassa); "Excluded Volume Effects and Binary Cluster Integrals in Dilute Polymer Solutions" (Yamakawa); "Experimental Study of the Influence of Specific Intramolecular Interactions on the Conformation of Model Molecules (Peptides and Oligopeptides)" (Néel); "Thermodynamic Parameters of Helix-coil Transitions in Polypeptide Chains" (Ptitsyn); "Thermodynamic Properties of Liquids Including Solutions—Dependence of Polymer Properties on Molecular Properties" (Huggins); and "Molecular Clustering and Segregation in Sorption Systems" (Lundberg).

Thus, the reader will find gathered in this volume current reviews of two diverse aspects of polymer science: one of them a most popular area of study today and the other a discipline that began with some of the first quantitative physical studies of macromolecular systems and perhaps reached a peak of activity two decades ago. These articles are evidence that equally challenging questions mark the frontiers of both the relatively new field and the more "classical" one.

Anyone interested in morphology or solution thermodynamics of polymers will find this book a convenient source of information and of selected references to the relevant original literature. But potential readers (and librarians) should take note that all these papers have appeared previously in the IUPAC journal Pure and Applied Chemistry, Volume 31 (1972).

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Progress in Polymer Science Japan, Volume 5. K. Imahori and S. Murahashi, Eds., Halsted Press, New York, 1973. 308 + ix pp. $17.50

In this fifth volume of the series, the first three chapters are concerned with polymer synthesis and the remaining two with the properties of polymers.

J. Furukawa of Kyoto University gives the reader an excellent presentation of vinyl polymerizations, which yield alternating copolymers, and the mechanisms which have been written to explain these polymerizations. This first chapter, "Alternating Copolymers of Diolefins and Olefins Compounds," is well written and comprehensive in that it presents a critical survey of the author's work as well as the work of other major contributions to this area. Only in a few places are some of the presentations of mechanisms or the explanations of supporting data not quite as clear as they might be --- eg., the interpretation of the NMR spectra of growing methylmethacrylate chain (drawings on p. 10) and the explanation of orbital overlap in the Diels-Alder reaction (frontier electron approach on p. 37).

In Chapter 2, "Studies on Poly-α-Amino Acids," J. Noguchi of Hokkaido University provides an interesting survey of work which includes the synthesis of poly-α-amino acids and their catalytic activity, as well as the spinning of poly-α-amino acids and the properties of the fibers obtained. Of the 78 pages in the chapter, 53 are devoted to a discussion of research on the catalytic activity of poly-α-amino acids as models for enzyme active sites. In most cases, the catalytic reaction studied is the hydrolysis of p-nitrophenyl acetate. It is apparent from the discussion that the scientific information obtained on the nature of the enzyme active site has been proportionately low compared to the research effort which has been expended.

Chapter 3 is an interesting, well written discussion of "Four-Center Type Photopolymerization in the Crystalline State," by M. Hasegawa, Y. Suzuki, H. Nakanishi, and F. Nakanishi of the Research Institute for Polymers and Textiles, Yokohama. This chapter covers the authors' work in the 2 X 2 photo cycloaddition reactions of diolefins in the crystalline state which yield crystalline polymers. A clear outline of the features of these topochemical polymerizations and the conditions which are necessary for such polymerizations to take place make this chapter required reading for those interested in this intriguing area.

Of the two chapters dealing with the physical chemistry of polymers, the first is by M. Kaneko of Hokkaido University and is entiteled "Viscoelastic Properties of Dilute Polymer Solutions." After a brief survey of theoretical concepts, extensive experimental results are presented, and then interpreted in terms of the appropriate molecular theories of viscoelasticity. Such correlation of theory and experiment can give much useful information on both intramolecular and intermolecular interactions in polymers, and the methods and conclusions described in this chapter will be of interest to a variety of polymer chemists, physicists, and engineers.

The second of these chapters, "Transport Processes in Charged Membranes," is by Y. Kobatake and N. Kamo, also at Hokkaido University. The focus of this article is the explanation of transport phenomena occurring in membranes by means of the thermodynamics of irreversible processes. The approach and results presented here really have very little to do directly with polymers per se, but membranes are so important in a number of areas of interest to polymer scientists (e.g., water desalination, life processes) that this review will almost certainly have a sizable audience, nonetheless.

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The *Journal of Polymer Science* publishes results of fundamental research in all areas of high polymer chemistry and physics. The *Journal* is selective in accepting contributions on the basis of merit and originality. It is not intended as a repository for unevaluated data. Preference is given to contributions that offer new or more comprehensive concepts, interpretations, experimental approaches, and results.

In addition to meeting these standards for excellence and significance, manuscripts for the *Polymer Letters Edition* must exhibit a special degree of novelty and timeliness that warrants speedy publication, even in brief preliminary form. Short contributions that do not in the opinion of the editors meet this test, but are otherwise acceptable, will be published as *Notes* in the *Polymer Chemistry* or *Polymers Physics Editions.*

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Detailed instructions on preparation of manuscripts are given frequently in the *Polymer Chemistry* and *Polymer Physics Editions.*

Polymer Letters Edition

October 1973 Volume 11 Number 10

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Journal of Polymer Science: Polymer Letters Edition

The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition*, monthly; *Polymer Physics Edition*, monthly; *Polymer Letters Edition*, monthly; *Polymer Symposia*, irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition*, *Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

STRUCTURE OF CELLULOSE ACETATE DESALINATION MEMBRANES

Molecular orientation in films of cellulose acetate has been detected by several investigators using birefringence measurements (1,2,3). However, the membranes studied by these investigators were not the asymmetric desalination type membrane. The references cited were in the literature nearly a decade before Loeb and Sourirajan published their procedure for preparing modified cellulose acetate desalination membranes which possess both high salt rejection and high water flux properties.

It appears that the most natural molecular configuration or orientation is for the polymer chain molecules to lie in the plane of the membrane. However, if acetone is sorbed and desorbed from a cellulose acetate membrane, there is some evidence (1) to indicate that the molecules tend to orient perpendicular to the surface of the membrane. It is not evident from the literature that anyone has directly related either type of orientation to the performance characteristics of reverse osmosis membranes. It was the objective of this study to determine if such polymer orientation is a factor influencing the flux and salt rejection properties.

Cellulose acetate desalination membranes prepared by either the Loeb and Sourirajan (L-S) (4) or Manjikian et al. (Mj) (5) procedures require an optimum evaporation time in order to obtain good performance characteristics (6). The optimum evaporation time was confirmed for the membranes used in this study, using the Mj formulation and procedure, as shown in Figure 1.

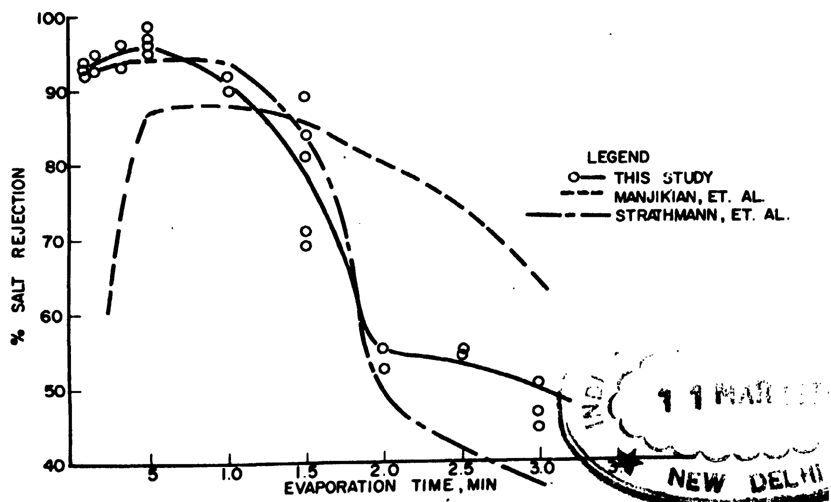

Figure 1

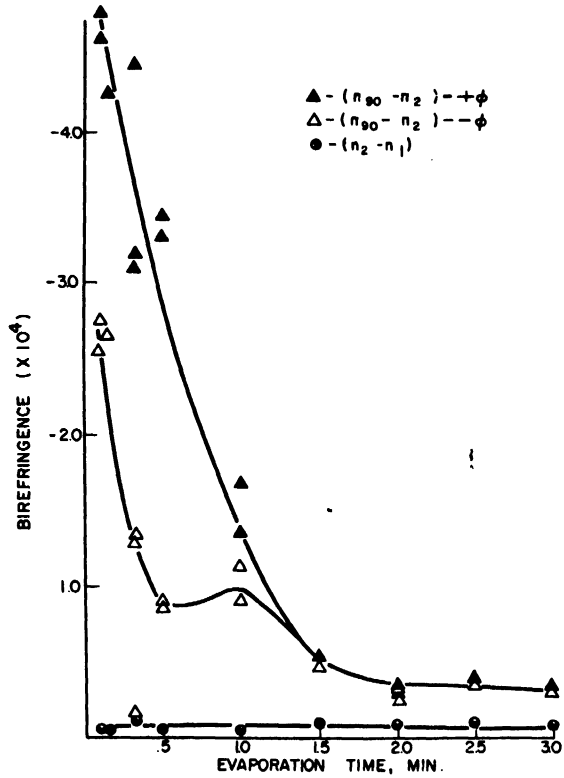

Figure 2

Birefringence measurements were made of a series of unannealed Mj-type desalination membranes prepared using different evaporation times. Each membrane was held between two stainless steel picture frames. The frame containing the secured membrane was attached to a simplified goniometer. The axis of rotation of the goniometer was perpendicular to the direction of the incident beam. The goniometer arrangement was such that three positions, corresponding to angles of +60, –60, and 0° (flat) between the incident beam and the normal to the membrane, could be measured reproducibly. The goniometer device was positioned on a strain-free, optically-ground glass plate which was sealed to the bottom of a flat-bottom glass dish. The goniometer fitted tightly into the cavity on the bottom of the dish to prevent the goniometer from moving during the rotation of the dish on the microscope stage. This goniometer arrangement allowed the membrane to be immersed completely in water while the birefringence measurements were being made. This experimental precaution of keeping the membrane wet while measurements were being made was found to be very important since it was established that structure-property relationships were very sensitive to even minor degrees of dehydration. The birefringence of the membrane for an incident beam parallel to the film

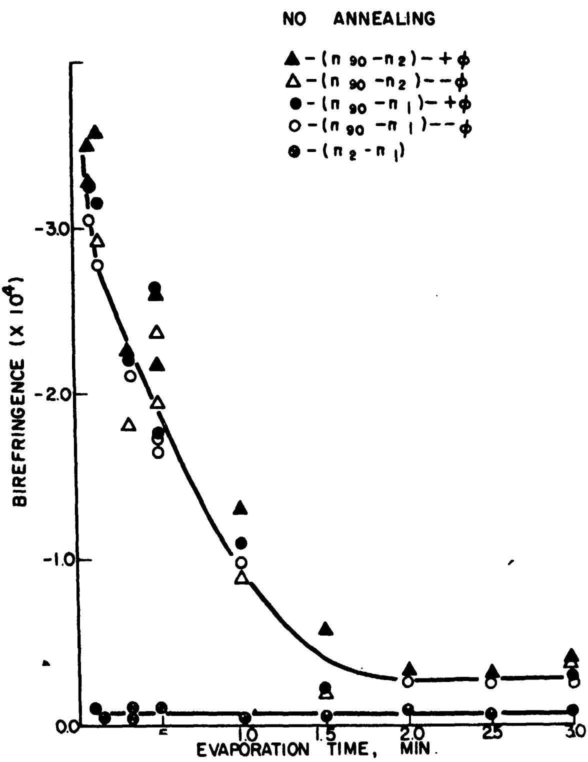

Figure 3

surfaces was calculated by an extrapolation method developed independently by Spence (3) and by Stein (7). The results of these measurements are presented in Figure 2. It can be shown that the large negative birefringence at low evaporation times for the tilted samples results from a significant amount of random orientation in the plane of the membrane. The birefringence of the tilted samples was found to increase in positive magnitude with an increase in evaporation time, indicating that molecular orientation is developing in a direction perpendicular to the membrane surface.

The changes in orientation of unannealed membranes is instructive but does not relate directly to the usual annealed membranes used for desalination. Similar measurements, using annealed samples of the same membrane series prepared at different evaporation times, showed that an optimum orientation was developed. The results shown in Figure 3 are for a tilt axis parallel to the draw direction used in the initial film casting step of the membrane fabrication.

An orientation factor F_ϕ useful in the interpretation of these results is defined as the difference in birefringence determined at the same tilt angle ϕ but in different directions, divided by the average of these birefringences:

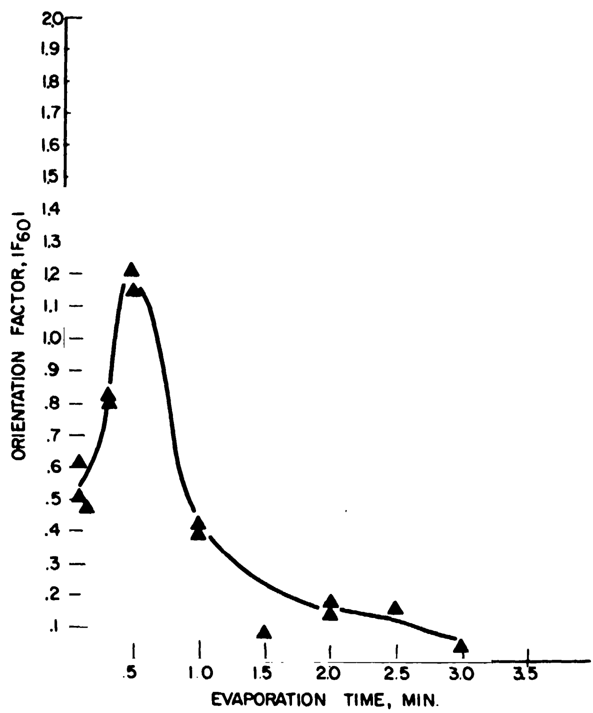

Figure 4

$$F_\phi = \frac{(n_{+\mu} - n_1) - (n_{-\mu} - n_1)}{[(n_{+\mu} - n_1) + (n_{-\mu} - n_1)]/2} \qquad (1)$$

where n_μ is the index of refraction of a refracted light ray in the membrane at an angle $\pm\mu$ from the normal to the surface of the membrane, corresponding to a $\pm\phi$ tilt angle, and n_1 is the index of refraction of a light ray vibrating in a direction effectively parallel to the tilt axis of the sample.

The maximum of the orientation factor seen in Figure 4 at a 0.5 minute evaporation time can be related to a maximum molecular orientation-angle perpendicular to the surface of the membrane (8). The fact that the maximum salt rejection correlates with the maximum of the orientation factor is taken as an indication that the most efficient desalination membrane requires an optimum orientation of structure perpendicular to the surface.

The development of orientation in the membrane must arise during certain stages of the membrane fabrication procedure. The usual procedure involves the steps of casting-solution formulation, casting the solution into a film using a Gardner knife, an initial evaporation of volatile solvent, quenching in an ice water bath with subsequent leaching, and a final annealing at a higher temperature. The detailed procedure used in this study is that described by Manjikian (5).

From an analysis of these steps, it was concluded that orientation perpendicular to the surface could be expected to be the result primarily of three causes: 1. the loss of volatile solvent (acetone) during the initial evaporation time; 2. membrane shrinkage; and 3. solvent removal faster than water entry during quenching and leaching.

The present evidence indicates that the most probable major cause of orientation is the loss of acetone during the evaporation step. Dreschel, et al. (1), found that orientation perpendicular to the surface of cellulose acetate membranes resulted during successive sorption-desorption of acetone vapor by a dry film. The differential swelling or momentum transfer from diffusing solvent may have a pronounced effect on polymer structure. Kopeck and Sourirajan (9) also found that the salt-rejection capabilities of normally prepared cellulose acetate membranes could be improved by a pretreatment involving reverse water flow through the membrane, i.e., in the same direction as acetone evaporation during the initial preparation procedure.

Several other experimental results tend to support the supposition that the observed orientation is a factor affecting the transport properties of the cellulose acetate desalination membrane. For example, the occurrence of such structural changes is also shown by the results of argon laser Raman spectroscopy studies (8) in addition to the birefringence measurements.

An initial interpretation of the results has led to the development of a proposed mechanism to explain the nature of each step in the membrane preparation sequence as it effects membrane structure (8). The probable mechanism for water transport in cellulose acetate membranes is considered to involve an aligned ice-like hydrogen bonding system not inconsistent with hydrogen-bonded water bridges between adjacent cellulose acetate molecules. Salt transport is considered to involve mainly either "activated" or "capillary" diffusion depending on the annealed condition of the membranes. It is anticipated that the overall mechanism for transport, based on the occurrence of polymer orientation predominantly perpendicular to the membrane surface, may serve as a useful guide for the preparation of more efficient desalination membranes.

The partial support of this study by the Office of Saline Water is gratefully acknowledged.

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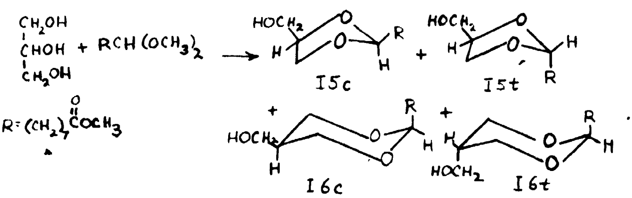
Received March 5, 1973
Revised July 30, 1973

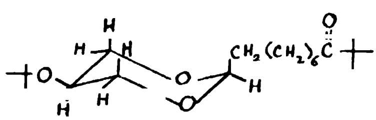
POLYMER LETTERS EDITION VOL. 11, PP. 609–612 (1973)

CRYSTAL STRUCTURES OF POLY(ESTER ACETALS) OF METHYL AZELAALDEHYDATE GLYCEROL ACETALS

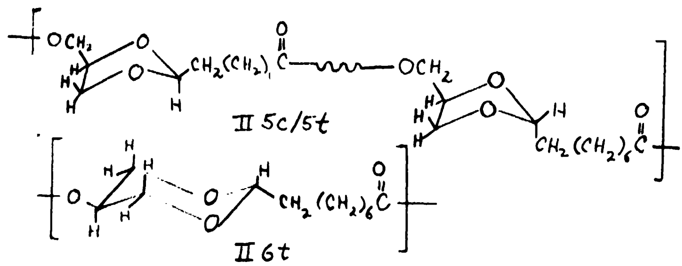
Recent investigations in our laboratory on the homogeneous and heterogeneous reactions (1) of copolyesters prepared from the four geometric isomers of methyl azelaaldehydate glycerol acetal made it of interest to us to determine, if possible, the crystal unit cell structure and dimensions of the four different ester-acetal homopolymers. The four isomeric repeating units consist of the cis (c) and trans (t) structures of both the five (dioxolane, I 5) and six (dioxane, I 6) member internal cyclic acetals within the ω-hydroxyester monomers (I) obtained from the reaction of glycerol with methyl azelaaldehydate dimethyl acetal (2) as follows:



Crystal structure determinations on the homopolyesters obtainable from these monomers was accomplished by first separating the cyclic acetal monomers by preparative gas-liquid chromatography and then polymerizing each fraction individually to prepare the homopolyesters (2). Unfortunately, it was not possible to obtain a clean separation of I 5c and I 5t, so only a copolymer could be prepared of these two monomers. In contrast, monomers I 6c and I 6t were readily obtained in high purity, and the homopolymers, II 6c and II 6t, which were prepared under conditions which did not permit isomerization, had considerably higher degrees of crystallinity than the II 5c/5t copolymer. It should be noted in this regard, however, that analytical gas-liquid chromatography studies indicated that the ratio of I 5c to I 5t in the fraction obtained by preparative GC was generally between 1.5 and 2, so that the copolymer prepared from these two substitutional isomers presumably could have contained only cis unit crystalline regions. The three poly(ester acetals) studied, therefore, had the following repeating unit structures:



II 6c



X-ray diffraction data used for calculating the crystal unit-cell dimensions were obtained from powder patterns of polymers II 6 c and II 6 t and from copolymer II 5c/5t. Annealed samples of the two homopolymers gave 15-20 measurable lines, while the powder pattern of the copolymer, which was unaffected by annealing, consisted of only 6 detectable lines. An interesting feature of the powder photographs of some of the samples of all three polymers was that the patterns contained spots despite rotation of the specimen during exposure. This observation indicates that the crystallites present had at least one dimension of the order of the 10^{-3} to 10^{-4} cm., presumably folded-chain lamellae, which is not unexpected in polymers of this type.

Indexing of the crystalline structure of the polymers based on these powder patterns is probably accurate only to 0.02°θ, and the Lipson method (3) was used for this purpose. The indexing was aided by the close correspondence between the c parameters and the repeat distances calculated for the three monomer residues. The lattice constants determined for the three polymers are shown in Table I, and the observed (d_o) and calculated (d_c) d spacings are listed in Table II, from which it can be seen that the agreement is generally quite satisfactory.

The unit cell parameters were also used to calculate the theoretical density of the completely crystalline polymers, and these values were compared to experimentally-determined density values in order to calculate degrees of crystallinities of the samples studied. This information is compiled in Table III, in

TABLE I

Lattice Constants Calculated for 6-Member Cyclic Acetal Homopolymers and 5-Member Cyclic Acetal Copolymer[a]

Repeat Unit in Polymer	Designation	System	a(Å)	b(Å)	c(Å)	γ
cis-6-ring	II 6c	monoclinic	7.842	5.476	12.34	96°.45'
cis/trans-5-ring	II 5c/5t	orthohombic	7.367	5.186	13.52	-
trans-6-ring	II 6t	orthohombic	7.487	5.117	13.56	-

[a]Estimated limits of error are ± 0.005 Å for a and b axes, and ± 0.01 Å for c axis.

TABLE II

Observed (d_o) and Calculated (d_c) d Spacings of Crystalline Homopolymers and Copolymers

Line No.	Cis-6-ring Unit; II 6c Int.	d_o	d_c	hKl	Cis/Trans-5-ring Unit; II 5c/t Int.	d_o	d_c	hKl	Trans-6-ring Unit; II 6t Int.	d_o	d_c	hKl
1	mb	12.6	12.3	001	ms	13.8	13.5	001	m	13.6	13.6	001
2	w	7.8	7.8	100	wb	7.4	7.4	100	wb	7.2	7.2	100
3	v^2w	5.44	5.44	010	sb	4.242	4.240	110	vsb	4.220	4.224	110
4	m	4.72	4.73	$1\bar{1}0$	vw	3.371	3.381	004	v^3w	3.867	3.869	103
5	vs	4.417	4.414	$1\bar{1}1$	vs	3.138	3.089	113	m(sp)	3.022	3.021	210
6	s	4.226	4.231	110	s	3.040	3.003	210	vw	2.500	2.496	300
7	mb	3.893	3.894	200	mb	2.679	2.673	{114, 005}	vw	2.407	2.409	{120, 015}
8	wb	3.493	3.490	112	vw	2.455	2.456	300	v^2w	2.286	2.283	115
9	vwb	3.064	3.063	{004, 210, $1\bar{1}3$}	vwb	2.232	2.232	{214, 310}	v^2w	2.199	2.197	205
10	v^2w	2.870	2.869	104	v^2wb	2.111	2.109	312	mb	2.096	2.100	{221, 220}
11	v^2w	2.687	2.684	014	v^2w	1.922	1.919	223	vw	1.914	1.914	223
12	v^3wb	2.540	2.540	301	v^3wb	1.872	1.872	025	w	1.870	1.871	{314, 400}
13	v^3wb	2.397	2.401	{$3\bar{1}1$, 302}	v^3wb	1.549	1.544	226	v^2wb	1.666	1.669	{306, 130}
14	v^2w	2.286	2.283	$3\bar{1}2$					v^2wb	1.603	1.603	{018, 033}
15	v^3w	2.225	2.225	{$2\bar{3}2$, $1\bar{2}3$}					v^3w	1.525	1.524	034
16	v^3w	2.191	2.192	{$1\bar{1}5$, 303}								
17	v^3w	2.105	2.107	312								
18	v^3wb	2.008	2.001	222								
19	v^3w	1.924	1.923	401								
20	v^3w	1.875	1.876	$2\bar{2}4$								
21	v^3w	1.742	1.742	$3\bar{1}5$								
22	v^3wb	1.626	1.624	413								

TABLE III

Calculated and Observed Densities of Crystalline Homopolymers and Copolymer

Repeat Unit in Polymer	Designation	Density[a] Observed	Density[a] Calculated	Percent Crystallinity
cis-6-ring	II 6 c	1.182	1.439	32
cis/trans-5-ring	II 5c/5t	1.135	1.465	15
trans-6-ring	II 6t	1.174	1.457	28

[a]Density of completely amorphous material is 1.093 for copolymer of all four units.

which the calculated density is based on the assumption that there are two repeat units in each unit cell. The much lower degree of crystallinity observed for the copolymer in this table agrees with the results obtained by other methods of crystallinity determination, namely by X-ray diffraction patterns and differential scanning calorimetry.

The lattice parameter data of Table I indicates that all three polymers crystallized in a unit cell which can be considered to be a modified polyethylene unit cell, with the c parameters approximately equal to the monomer repeat distances in each case. Homopolymer II 6t and the copolymer II 5c/5t have a and b parameters which are distorted from the polyethylene case in that their magnitudes are somewhat greater, and the ratio of a:b is about 4% different from the value of the square-root of 2 which is found in polyethylene. Homopolymer II 6 c showed an even greater deviation in these parameters and the symmetry of the system is reduced, which is consistent with the expected greater bulkiness of this type of ring structure containing an axial substituent.

The agreement between the c parameters and the calculated monomer repeat distances indicates that the polymer crystallized in a planar conformation, while the width of the diffraction lines and the spherulitic morphology observed for these crystalline polymers clearly indicate that folded-chain structures were involved.

For X-ray analysis, powder photographs were taken using an 11.67 cm diameter Philips Debye-Scherrer Camera, and the films were measured using a Philips film-measuring device.

The authors are grateful to the National Science Foundation for the support of this work.

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POLYMER LETTERS EDITION VOL. 11, PP. 613-617 (1973)

RADIATION-INDUCED CROSSLINKING OF POLYETHYLENE IN THE PRESENCE OF VARIOUS ACETYLENIC COMPOUNDS

Polyethylene is well known to undergo intermolecular crosslinking as a result of the influence of ionizing radiation (1). The efficiency of the reaction is rather low depending on the chemical structure and the physical state of the polymer. The G values of the crosslinking have been reported to be about 1.0-2.5 (2-9). Recently, it was found that the crosslinking reaction was markedly promoted in the presence of acetylene (10) or in mixtures of acetylene and tetrafluoroethylene (11). However, the mechanism of the promotion is not yet clear, and the effect of higher acetylenic derivatives has not been reported.

In this work, the crosslinking reaction of polyethylene was investigated by exposing its film samples to ^{60}Co γ-rays in the presence of acetylene or its higher (C_3-C_5) derivatives. A study was made also of the reaction in the presence of some fluorinated acetylenes.

Experimental

The polyethylene (Hizex 2200P) was moulded at 140°C into a film about 0.2 mm thick. The film samples were degassed under a pressure of 10^{-4} mm Hg for 15 hr in glass ampules. Irradiation by γ-rays was carried out in vacuum or in an atmosphere of $CH{\equiv}CH$, $CH{\equiv}CCH_3$, $CH{\equiv}CC_2H_5$, $CH{\equiv}CC_3H_7$, $CH_3C{\equiv}CC_2H_5$, $CH{\equiv}CCF_3$ (TFMA), or $CF_3C{\equiv}CCF_3$ (PFB). These additives, which had been purified by the alternate freezing and thawing technique under reduced pressure, were charged in until the total pressure reached 2 kg/cm^2 at room temperature. The γ-rays used were from 120,000 curies of ^{60}Co, and the irradiation was carried out at room temperature with a constant dose rate of 1×10^6 rad/hr for 4-130 hr.

The irradiated ampules were allowed to stand in the dark at room temperature for 40 hr before opening. The film samples were degassed under the reduced pressure of 10^{-3} mm Hg for 20 hr and weighed in order to determine the change in weight. They were immersed in boiling xylene for 20 hr and then in methanol for 4 hr, and dried in vacuum for 20 hr at room temperature. The insoluble gel fraction was determined by measuring the weight per cent of the residue.

Infrared spectra of the irradiated polyethylene were measured with a Hitachi-Perkin Elmer infrared spectrophotometer, model 225. The amount of unsaturation was determined from the absorbance at 966 (trans vinylene), 910 (terminal vinyl), and 890 (vinylidene) cm^{-1} (12).

TABLE I

The Results of the γ-Ray Irradiation in the Presence of Various Acetylenic Compounds

Additives	Dose (Mrad)	Weight increment (wt %)	Gel fraction (wt %)	Terminal vinyl (No./1000C)	Trans vinylene (No./1000C)	Vinylidene (No./1000C)
Non-irrad, vacuum	-	-	0.0	0,00	0,01	0.06
	4,0	-	15,4	0,00	0,11	0.06
	6,0	-0,1	23,2	0,01	0,14	0.06
	16,0	-0,4	45,5	0,00	0,31	0.05
	20,0	-	49,9	0,01	0,41	0.05
Acetylene	4,0	-	59,2	0,07	0,11	0.05
	6.0	0.32	69,2	0,16	0,08	0.03
	16.0	0,70	81,7	0,34	0,27	0.04
	20.0	0,81	83,5	0,48	0,36	0.06
Methyl-acetylene	6.0	0,50	13,9	0,03	0,21	0.03
	16.0	0,70	34,0	0,04	0,49	0.05
	20,0	0,80	44,0	0,05	0,59	0.06
Butyne-1	5,0	0,31	0,9	0,05	0,24	0.06
	16,0	0,60	8,7	0,04	0,50	0.05
	20,0	0,91	15,5	0,03	0,63	0.07
	67,0	-	51,6	0,02	1,07	0,13
	107,5	-	73,6	0,09	1,91	0,14
Pentyne-1	5,0	0,30	1,0	0,00	0,13	0,02
	16,0	-	11,1	0,03	0,44	0,07
	20,0	1,30	9,8	0,04	0,60	0,10
	67,0	-	46,6	0,08	1,64	0,19
	107,5	-	65,3	0,08	2,31	0,18
Pentyne-2	20,0	0,68	0,3	0,00	0,38	0,00
	67,0	-	14,6	0,00	1,03	0,04
	107,5	-	40,9	0,04	1,40	0,04
	128,5	-	47,7	0,05	2,01	0,10
TFMA	4,0	-	7,2	-	-	-
	6,0	-	42,0	-	-	-
	16,0	-	58,3	-	-	-
	20,0	-	66,8	-	-	-
PFB	4,0	-	30,4	-	-	-
	6,0	-	46,4	-	-	-
	16,0	0,62	57,5	-	-	-
	20,0	1,02	73,0	-	-	-

TFMA: trifluoromethylacetylene; PFB: perfluorobutyne-2. Conditions: dose rate, 1 X 10^6 rad/hr; temperature, ca. 25°C.

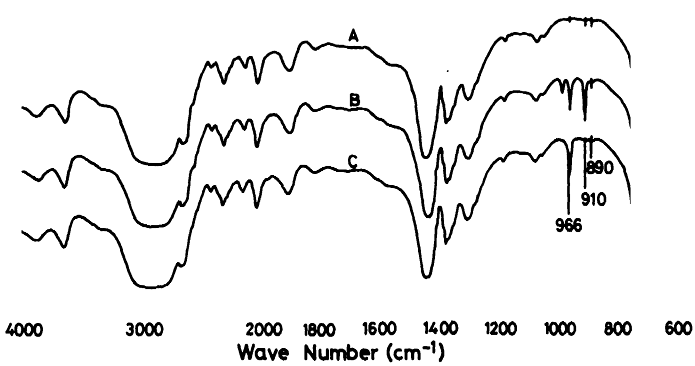


Fig. 1. Infrared spectra of polyethylene: A, non-irradiated; B, irradiated in acetylene; C, methylacetylene.

Experimental Results

The results of the irradiation are summarized in Table I.

As can be seen in Table I, the polyethylene films decreased in weight when irradiated in vacuum, but increased in weight in the presence of the additives. A change in weight was not observed when polyethylene was treated without the irradiation of γ-rays. It is evident that gel formation is accelerated by the addition of acetylene, TFMA, and PFB. In contrast, it is depressed by methylacetylene, butyne-1, pentyne-1, and pentyne-2.

The infrared spectra of polyethylene shown in Figure 1 are non-irradiated (A), irradiated in acetylene (B) and irradiated in methylacetylene (C). The significant difference in these spectra is that the irradiated polyethylene shows new absorption peaks at 910 cm^{-1} (terminal vinyl), and 966 cm^{-1} (trans vinylene). Especially, in acetylene, the terminal vinyl increased markedly, while in methylacetylene the increase in trans vinylene was significant. The amounts of both types of unsaturation were found to increase almost linearly with the radiation dose in every case although in cases of fluorine containing derivatives, unsaturation was not quantitatively determined owing to the overlap of the peaks with those of C–F bonds. In these infrared spectra and those obtained with other acetylenic compounds, the formation of the conjugated double bonds (1580–1650 cm^{-1}) and the tri-substituted vinylene can not be found.

By comparing with each other, the following facts become evident from the results. 1. Formation of crosslinking and terminal vinyl increase markedly, but that of trans vinylene decreases in the atmosphere of acetylene relative to irradiation in vacuum. On the other hand, 2. formation of crosslinking decreases in C_3–C_5 derivatives. 3. In the fluorine containing derivatives, formation of crosslinking increases.

Discussion

Although it is rather speculative, we, based on the experimental results presented above, propose the following chain scheme for the reaction in the presence of acetylenic compounds.

1) initiation

$$\sim CH_2 \sim \rightsquigarrow \sim \dot{C}H \sim + \dot{H} \qquad (1)$$

$$\sim CH_2 - CH_2 \sim \rightsquigarrow 2 \sim \dot{C}H_2 \qquad (1)$$

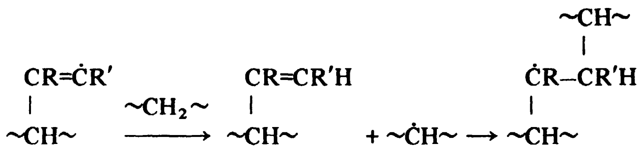
2) propagation

2-1) addition of acetylenic compounds

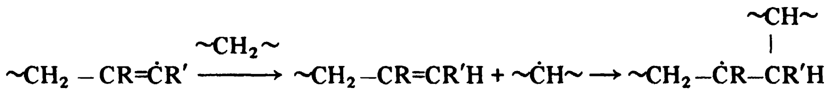
$$\sim \dot{C}H \sim + CR{\equiv}CR' \longrightarrow \sim \overset{\overset{\displaystyle CR{=}\dot{C}R'}{|}}{C}H \sim \qquad (2)$$

$$\sim\dot{C}H_2 + CR{\equiv}CR' \longrightarrow \sim CH_2{-}CR{=}\dot{C}R' \qquad (2)'$$

2-2) crosslinking and endlinking

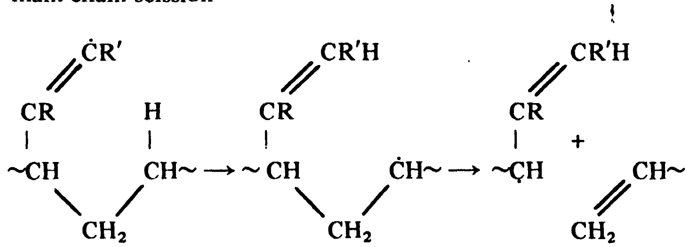


(3)



(3)'

3) main-chain scission



(4)

In the above scheme, the reaction may be initiated by the formation of the polymer radicals resulting from the dissociation of C–H or C–C bonds of polyethylene during the irradiation. The addition of the acetylenic compounds to initial polymer radicals is evident from consideration of the observations that the weight of polyethylene decreases in vacuum, but that it increases in the presence of the additives. As pointed out earlier, the trans vinylene formation decreases in acetylene and the infrared spectra of the polymers irradiated in acetylene or methylacetylene (Fig. 1) do not show the existence of the conjugated or tri-substituted unsaturation. The absence of tri-substituted unsaturation was also observed in the case of TFMA. From these results, it may be said that the crosslinking through the combination between two vinyl type radicals, or between the vinyl type radical and the initial polymer radical is negligible. Hence, we assume that the crosslinking in the presence of acetylenic compounds may take place through the abstraction of a hydrogen atom from an adjacent polymer molecule and the addition of the resulting polymer radical to the olefinic bond (eq. (3)). Since the polymer radical is always regenerated in these steps, the crosslinking reaction proceeds through a chain mechanism. Equation (4) indicates that there may be some possibility of a intramolecular hydrogen abstraction, and a main-chain scission through the radical transition. It may be one reason why the formation of terminal vinyl increases in the presence of acetylene. However, in the case of the derivatives which carry alkyl groups, formation of crosslinking becomes smaller than those in vacuum and trans vinylene formation increases. In those cases, the vinyl type radicals may be deactivated by the abstraction of a hydrogen from the additives instead of polyethylene (eq. (5)).

4) deactivation of vinyl radical

$$\sim CR{=}\dot{C}CH_2R'' + CR{\equiv}CCH_2R'' \longrightarrow \sim CR{=}CHCH_2R'' + CR{\equiv}C\dot{C}HR'' \qquad (5)$$

On the other hand, in the case of fluorine containing derivatives, the above reaction does not occur because of the strong C—F bond, and the effect of these compounds may, therefore, be interpreted in the same way as stated for the case of acetylene.

The detailed results and discussions on the chain mechanism of the cross-linking will be reported later.

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Received March 26, 1973
Revised July 19, 1973

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POLYMER LETTERS EDITION VOL. 11, PP. 619–623 (1973)

APPLICATION OF THE LANTHANIDE SHIFT REAGENTS TO THE STUDY OF THE CONFORMATION OF STRUCTURALLY RIGID POLYAMIDES

Lanthanide shift reagents (LSR) have become a recognized technique in assignment of nmr spectra of complex organic molecules (1), and it has been recognized that the magnitude of the induced shift contains detailed information about the geometry of the lanthanide-substrate complex (2).

We have applied the LSR technique to the conformational study of a family of stereoregular polyamides and of their model diamides.

We have measured the Eu $(fod)_3$ induced shifts (3) of compounds collected in Table I, and these data have been used to determine the geometries of the relative Eu-amide complexes. The above geometries have been obtained by determining the optimal location of the Eu ion in the space around the amide oxygen atom according to a method described in detail elsewhere (4), and applying the equations of the lanthanide pseudocontact interaction (5).

Recent work (6) based on nmr data, dipole moments, and a priori conformational energy estimates, has shown that diamides I, III, V, and VI (Table I) all exist in a preferred conformation where the two diamide carbonyls lay close to each other, being almost eclipsed to the C_1-C_2 bond (Fig. 1).

Inspection of molecular models shows that only one $Eu(fod)_3$ molecule can possibly come in contact with the two carbonyls in such conformation. Assuming the same Eu-O distance (R = 3.0A°), Eu-O-C angle (ϕ = 120°) used previously (4) for other Eu-amide complexes and allowing only the Eu-O-C-N dihedral angle ω to vary, appropriate geometries for $Eu(fod)_3$ complexes could be obtained.

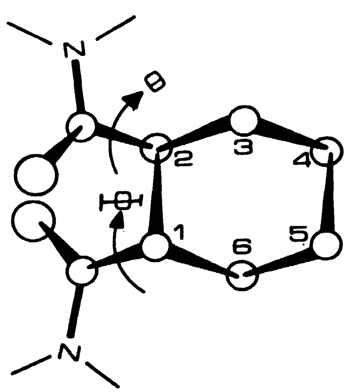
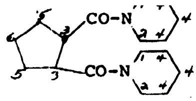
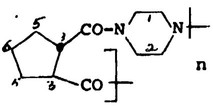
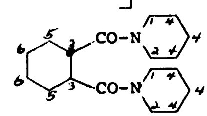
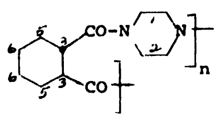
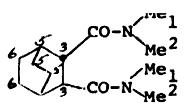
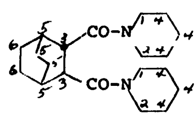
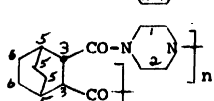


Fig. 1. Preferred conformation of diamide III. The Piperidine rings are omitted for clarity and only the cyclohexane ring is shown. The two C–O bonds are both almost eclipsed with respect to the C_1-C_2 bonds.

TABLE I

Effect of Eu(fod)$_3$ on the 60 MHz NMR Spectra of Model Diamides and Related Polymers and Molecular Geometry Parameters of the Corresponding Complexes[a]

N.	Compounds	1,2	3	5	6	R Å	[illegible]	[illegible]	Eu-Eu (Å)
I		3.66	3.66	1.90	1.90				
		4.4	13.5	5.6	3.0	3.0	120°	80°	3.0
		(3.3)	(13.3)	(5.1)	(2.5)				
II		3.90	3.90	1.91					
		9.0	20.6	6.5					
		-	--						
III		3.66	3.22	1.66					
		2.6	8.0	3.2		3.0	120°	80°	0
		(2.8)	(8.0)	(3.2)					
IV		3.80	3.20	1.80					
		5.0	10.3	3.2					
		—	—	—					
V		3.23 / 3.00	3.77	1.79					
		3.3	16.0	6.0		3.0	120°	80°	3.0
		(3.5)	(16.0)	(6.0)					
VI		3.66	3.84	1.66					
		2.3	14.5	5.7		3.0	120°	80°	3.0
		(1.9)	(14.4)	(5.0)					
VII		3.80	1.50	1.50					
		3.9	13.0	5.3					
		—	—	—					

[a]Only clearly detectable signals are reported; figures in the first row, underlined, indicate chemical shifts of the undoped spectra; figures in the second row indicate observed molar induced shifts; figures in the third row indicate calculated molar induced shifts.

In these complexes the Eu ion is considered alternatively bound to one oxygen atom so that an average deshielding effect of the Eu ion on each proton must be computed. In Figure 2 is shown, as an example, the spatial arrangement of this complex in the case of diamide III.

The distance between the two alternative locations (labeled Eu-Eu in Table I) is close to zero in this particular case, for diamides I, V, and VI a finite value is found (3.0 A°).

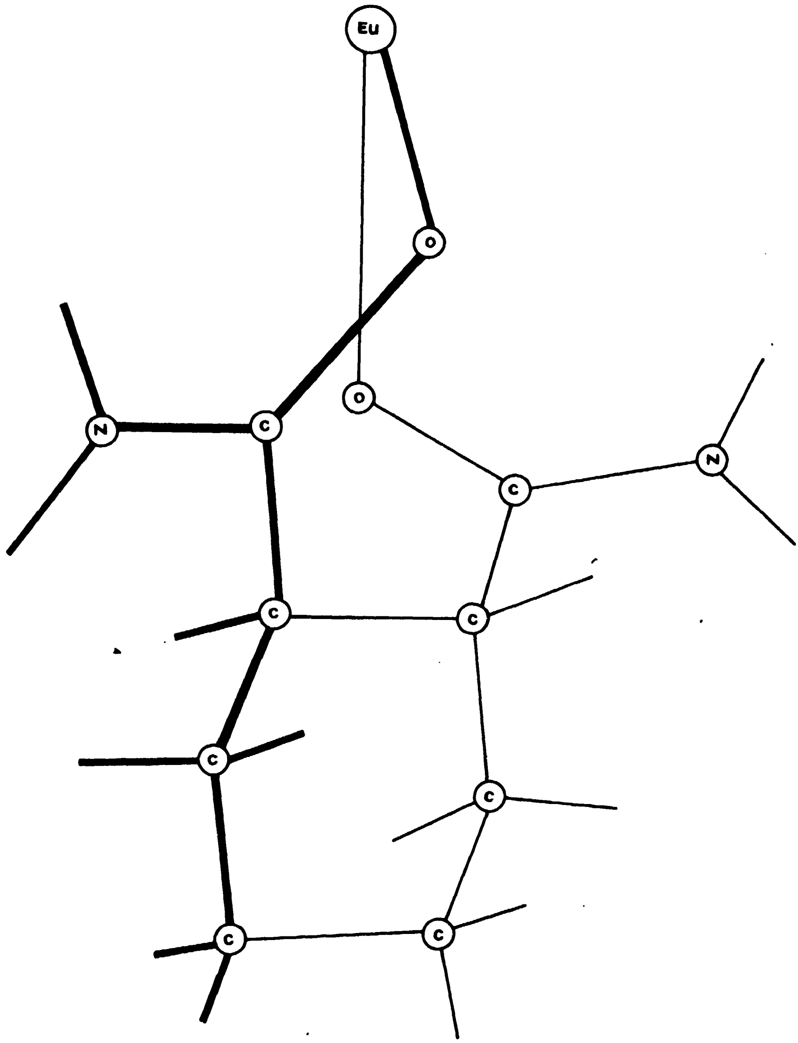


Fig. 2. Molecular geometry of the Eu(fod)$_3$-diamide III complex. Diamide III is represented in its preferred conformation (see also Fig. 1). Only one Eu ion is involved in the formation of this complex.

The geometry of the corresponding Eu(fod)$_3$-polyamide complexes, as deduced from the nmr induced shifts for the three polyamides stidied (Table I), is in agreement with the proposed (6) rod-like, extended conformation of these polymers (Fig. 3).

The nmr induced shifts for the N-methylene groups are found to be nearly doubled in the polyamides with respect to the model diamides (Table I), while the remaining signals are found more or less unaltered with respect to the cor-

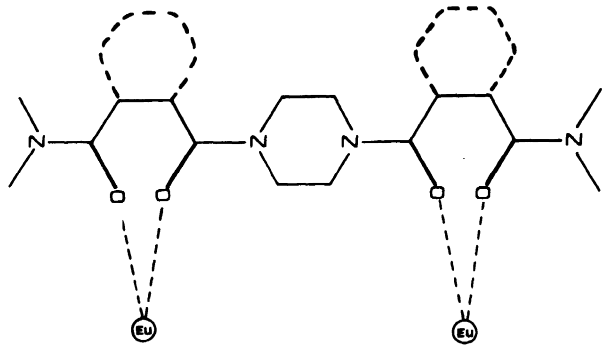


Fig. 3. Approximate molecular geometry of the $Eu(fod)_3$-polyamide complexes. The polymer chain is represented in its rod-like, extended conformation.

responding shifts in their model diamides. This indicated that in these (rod-like) complexes the Eu ions are located along the chain (Fig. 3) in such a way that each piperazine ring is shielded by two Eu ions.

If the polyamides in Table I existed in a coiled conformation, the carbonyl groups would be distorted from the "eclipsed" conformation in Figure 1 (leaving, eventually, room for two molecules of $Eu(fod)_3$ in the complex), so that one should expect marked deviations (4) from the shifts found above.

Although the conformation of our polyamides has been reasonably ascertained from other studies also, (6) it appears that the Eu-induced shifts data can be reasonably interpreted in support of the rod-like, extended structure shown in Figure 3.

Given the close structural analogy between our polyamides and polypeptidic biopolymers, it is possible that our findings may find useful applications in the study of the conformational properties and/or processes of some biological macromolecules.

The authors are grateful for financial support by the Department of the Army, Research Office–Durham, under Grant DAHCO–4–69–C–0050, and financial support from the Consiglio Nazionale Richerche of Italy.

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Received June 11, 1973
Revised July 20, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 625–629 (1973)

EFFECT OF STRONG ACIDS ON THE CIRCULAR DICHROISM SPECTRA OF STEREOREGULAR POLYAMIDES DERIVED FROM (+)-1,3-trans-CYCLOHEXANEDICARBOXYLIC ACID

We are currently investigating the effect of methanesulfonic acid (MSA) on the optical properties of some synthetic asymmetric polyamides and wish to report on some effects observed in the CD spectra of polyamides (1) derived from the acid (1,3-C_6) and either piperazine (PIP), trans-2,5-dimethylpiperazine (DMPIP), or N,N′-dimethylethylenediamine (DMED).

The CD spectra of these polyamides and the corresponding model diamide in trifluoroethanol (TFE) are shown in Figure 1. The overall spectral pattern is similar to that observed for related systems (2): the negative band at about 210-215 mμ can be assigned to the long-wavelength component of the split $n \rightarrow \pi^*$ amide transition, while the weaker positive band at about 225-230 mμ can be assigned to a $\pi \rightarrow \pi^*$ transition of the amide group (1,2). There are reasonable differences in intensity for the four curves described in Figure 1, but this point will be discussed later.

Addition of MSA results in drastic changes of the CD spectra of the model diamide, PIP and DMPIP polyamides, reported in Figures 2-4, respectively.

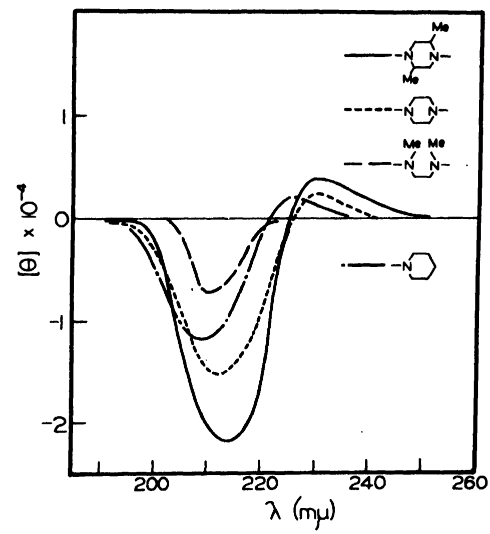

Fig. 1. CD spectra in TFE:DMPIP polyamide (————); PIP polyamide (-----); DMED polyamide (– – –); model diamide (– ——). Concentration $\sim 1.0 \times 10^{-2}$ mole amide residue/liter.

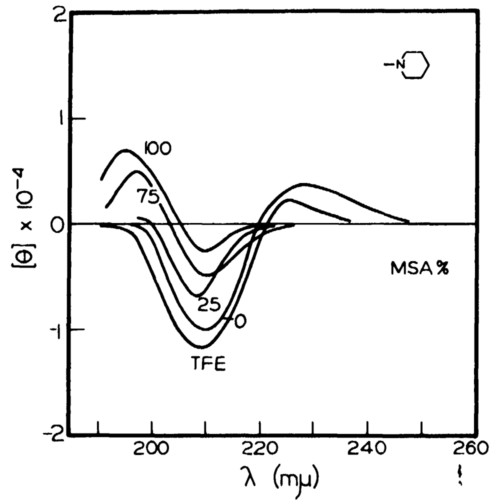

Fig. 2. CD spectra of model diamide in TMS/MSA mixtures. TMS = tetramethylenesulfone. Volume percentages are shown.

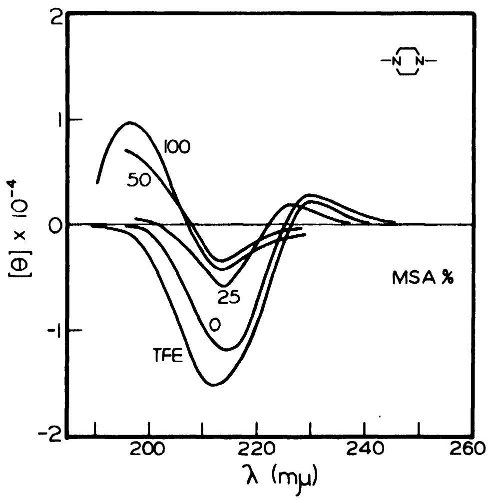

Fig. 3. CD spectra of PIP polyamide in TMS/MSA mixtures.

The $n \rightarrow \pi^*$ band at about 225-230 mμ disappears, the intensity of the 210-215 mμ band is greatly reduced, and a new band at 195-200 mμ emerges.

Protonation of the amide group at the oxygen atom seems to take place in strong acids (3), and both solvation and conformational effects may be responsible for the changes observed in the CD spectra (3). On the other hand, the spectral changes induced by MSA on the CD spectra of PIP and DMPIP polyamides (Figs. 3 and 4) reproduce closely to those already present in the spectrum of the model diamide (Fig. 2). We are therefore forced to conclude that

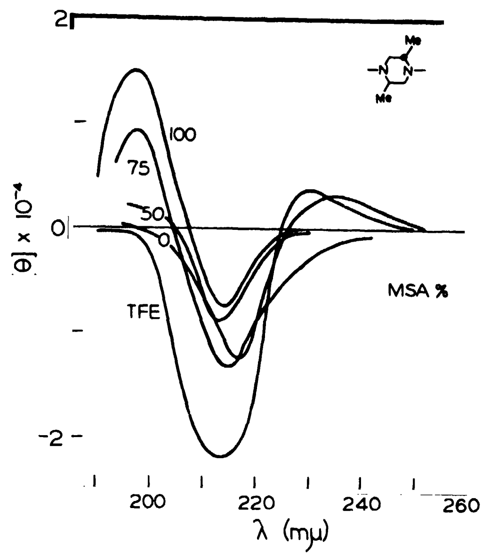

Fig. 4. CD spectra of DMPIP polyamide in TMS/MSA mixtures.

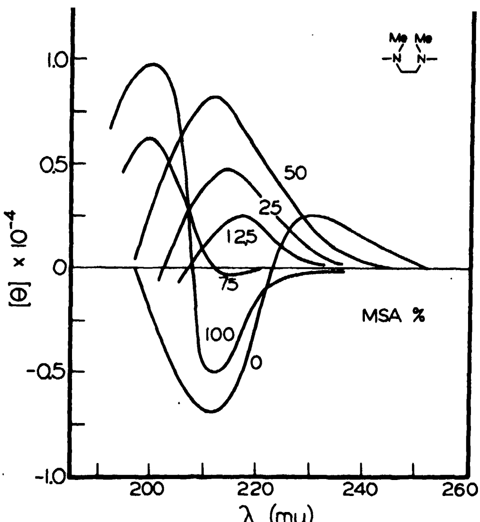

Fig. 5. CD spectra of DMED polyamide in TMS/MSA mixtures.

the appearance of the positive CD band at about 195-200 mμ does not reflect major conformational changes in these polymers.

Furthermore, inspection of molecular models shows that the 1,3-C_6 PIP and DMPIP polymeric chains tend to assume preferentially an extended rod-like conformation (4), and that amide groups are maintained in a somewhat rigid,

asymmetric environment in spite of the fact that the 1,3-trans-disubstituted cyclohexane ring is likely to experience a,e⇌e,a flipping. Optical properties result from short range interactions and it is not necessary to have perfectly ordered sequences in order to get coupling of identical chromophores with consequent enhancement of the rotatory strength (5). Increased rotatory strengths are actually observed for PIP and DMPIP polyamides with respect to the model diamide (Fig. 1) supporting this interpretation.

Addition of MSA results in even more complicated CD changes in the case of DMED polyamide (Fig. 5), and we interpret them as evidence of a conformational transition induced in this polymer by the strong acid effect.

The flexibility of the DMED backbone allows several arrangements of the polymer chain which is likely to behave as a random coil. In fact, the NMR spectrum of the DMED polymer shows the methyl resonances as a doublet (3.00 and 2.85 ppm, $CDCl_3$-TMS) indicating both cis and trans amide links, i.e., a lack of any preferred conformation in the polymer.

Protonation of amide units by MSA creates enough charge repulsion to cause a sizeable extension of the chains so that when the DMED polymer reaches the most extended form, its overall conformation should resemble those of PIP and DMPIP polyamides. In this process the amide units change their relative spatial positions along the polymer chain causing drastic changes in the CD spectrum (Fig. 5). The positive band at about 220 mμ, which appears at intermediate (10-50%) MSA concentrations is taken here as due mainly to the conformational changes above indicated. Solvation of the protonated amide chromophores occurs at higher MSA concentrations, so that the CD spectrum in pure MSA comes to resemble closely the PIP and DMPIP polymers (Figs. 3-5).

To our knowledge, relatively little experimental evidence is available at the moment on the respective roles that conformational and solvation processes may have in determining the CD spectral changes observed in polyamides and polypeptides in strong acids, and we feel that our findings may prove relevant in this respect.

The authors are grateful for financial support by the Department of the Army, Research Office-Durham, under Grant DAHCO–4–69–C–0050, and financial support from the Consiglio Nazionale Richerche of Italy.

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Received June 11, 1973
Revised July 20, 1973

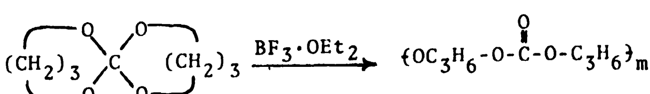
POLYMER LETTERS EDITION VOL. 11, PP. 631-633 (1973)

CATIONIC RING-OPENING POLYMERIZATION OF SPIRO-ORTHOCARBONATES

Some works have already been carried out on the ring-opening transfer polymerization of a spiro-orthocarboxylate, such as 1,4,6-trioxaspiro[4,4]nonane (1). In our recent publications (2), we established novel methods to prepare spiro-orthocarbonate derivatives as a new type of heterocyclic monomers from bis-organostannyl glycolate derivatives and carbon disulfide. In this report, we disclosed the mode of cationic ring-opening polymerization of spiro-orthocarbonates having five- to seven-membered rings.

Seven-membered spiro-monomer,1,6,8,13-tetraoxaspiro[6,6]tridecane(Ia;2 mol/1), was polymerized in the presence of a $BF_3 \cdot OEt_2$ catalyst (1.0 mol%) in dry ethylene dichloride at 30°C. After one hour, almost quantitative yield of tetrahydrofuran and the polycarbonate of 1,4-glycol (IIa;63-72% wt based on the monomer used) were formed: waxy solid having mean molecular weight by GPC 10,000; NMR(τ-value in $CHCl_3$, TMS as a standard) 5.83 (τ_{CH_2-O}, br. triplet, about 4H) 8.23 (τ_{CH_2-C}, br. triplet, about 4H) and IR($CHCl_3$) $\nu_{C=O}$ 1742 cm^{-1}, which was hydrolized to afford only 1,4-butandiol. These results suggest the polymerization with the elimination reaction of tetrahydrofuran.

Six-membered spiro-monomer,1,5,7,11-tetraoxaspiro[5,5]undecane (Ib), was polymerized analogously for 16 hr to give the polyethercarbonate (IIIb) in 91% yield; viscous material; mean molecular weight 5,600; NMR 5.76 (τ_{CH_2OCO}, br. triplet, 4H), 6.47 ($\tau_{CH_2OCH_2}$, br. triplet, 4H) and 8.06 (τ_{CCH_2C}, m, 4H); IR $\nu_{C=O}$ 1743, ν_{C-O} 1120 and 1035 cm^{-1}, forming bis(γ-hydroxypropyl) ether by basic hydrolysis at 100°C. Apparently, cationic polymerization of Ib was an example of 1,10-transfer polymerization as formulated in eq. (1).



(Ib) (IIIb) (1)

Five-membered spiro-monomer, 1,4,6,9-tetraoxaspiro[4,4]nonane was also polymerized, but more complicated results were obtained. A viscous polymer having molecular weight less than 6,000 (mean value 1,000) was obtained in 10-80% yield for 4-72 hour reactions. The polymer obtained showed two triplets at 5.71 and 6.31 assignable to τ_{CH_2OCO} and τ_{CH_2O} in the segment IIIc, respectively, and a sharp singlet at 6.37 assignable to polyethylene oxide unit IVc in the NMR spectrum, and $\nu_{C=O}$ at 1743 cm^{-1} and ν_{C-O} at 1108 and 1044 cm^{-1} in the IR spectrum. Ethylene carbonate was formed in the course of the polymerization reaction, and could not be polymerized under the

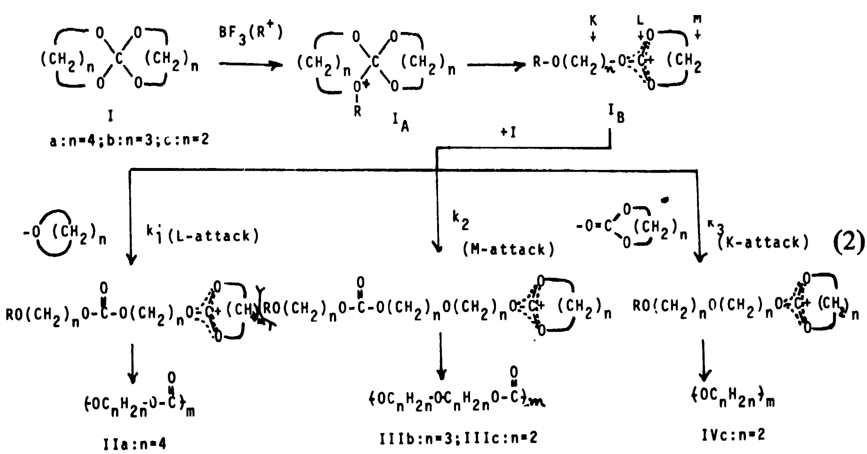
reaction condition. Diethyleneglycol was detected by VPC in the hydrolyzed products of the polymer formed, suggesting the partial occurrence of 1,8-transfer polymerization of Ic.

$$\text{-(-}OCH_2CH_2OCOOCH_2CH_2\text{-)}_n \qquad \text{-(-}CH_2CH_2O\text{-)}_m$$

(IIIc) (IVc)

Some efforts to promote exclusively 1,8-transfer polymerization were tried, but the ratio of IIIc- to IVc-content in the polymers formed remained in the range of 1.4-1.8 mol/mol as was calculated from the areas of τ_{CH_2OCO} (IIIc) and τ_{CH_2O} (IIIc + IVc).

Because acid-catalyzed decomposition of spiro-orthocarbonate to form cyclic carbonate and cyclic ether may, more or less, be possible (3), the reaction can proceed by alternative copolymerization or homopolymerization of the decomposition products to give polyethercarbonate(III), polycarbonate(II) or polyether(IV) units. However, we have tentatively formulated another polymerization courses, via the formation of a stable trioxocarbonium ion intermediate(I_B) followed by various bimolecular nucleophilic attacks on alkyl carbon atom K or M, and acyl carbon atom L in the ion I_B, with or without the elimination of inactive cyclic compounds, as shown in eq. (2)



(2)

The ring size of spiro-orthocarbonate strongly affected to the mode of the polymerization, that is, the seven-membered spiro-orthocarbonate reacted with the elimination of tetrahydrofuran and the formation of IIa($k_1 \gg k_2, k_3$). The six-membered spiro-orthocarbonate underwent a 1,10-transfer reaction ($k_2 \gg k_1, k_3$) exclusively. And, the five-membered compound underwent 1,8-transfer polymerization (k_2) accompanied by the formation of polyethylene oxide (k_3) and the elimination of ethylene carbonate ($k_2 \geqslant k_3 \gg k_1$).

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Received June 11, 1973
Revised July 26, 1973

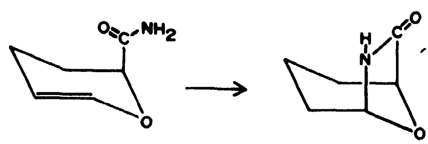
POLYMER LETTERS EDITION VOL. 11, PP. 635–637 (1973)

SYNTHESIS AND POLYMERIZATION OF 8-OXA-6-AZABICYCLO[3.2.1]OCTAN-7-ONE

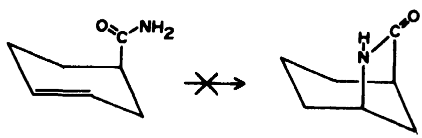
Many bicyclic lactams have been prepared by means of Beckmann rearrangement from bicyclic ketoximes (1,2), cyclization of amino carboxylic acids (3-7), and reduction of bicyclic imides (7-9), and their qualitative polymerizabilities have been studied (2,7).

We wish to report a synthesis of new bicyclic lactam ether, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (II) by intramolecular cyclization of 3,4-dihydro-2H-pyran-2-carboxamide (I).

Corresponding conversion of 3-cyclohexene carboxamide (III) to bicyclic lactam (IV) has never been accomplished (2).



I II



III IV

25.5g of I, prepared according to Whetstone and Ballard (10), and 5 ml of diethyl ether saturated with hydrogen chloride, were dissolved in an equivalent mixture of 380 ml of N,N-dimethylformamide and benzene, and then stirred on a steam bath at 90–95°C for two hours. After removal of solvents, distillation at 133° (4mm) in a nitrogen atmosphere gave 10.2g (40%) of a white waxy solid, II. Recrystallization from n-hexane gave a white fine needle crystal, m.p. 91–92°: infrared (CCl_4) 3180 and 3090 (νNH), 2955, 2920, 1721 (νC=O), 1468, 1420, 1330, 1280, 1248, 1077, 1068, 1034, 984, and 882 cm^{-1} (see Fig. 1): NMR (CCl_4) τ 7.9-8.6 (6H, $-CH_2-$), 5.90 (1H, $-\overset{|}{\mathrm{C}}\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$), 4.71 (1H, $-\mathrm{O}\overset{|}{\mathrm{C}}\mathrm{H}\overset{|}{\mathrm{N}}-$), and 1.61 (1H, $-\mathrm{NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$); mass spectrum (m/e) 127 (M^+).

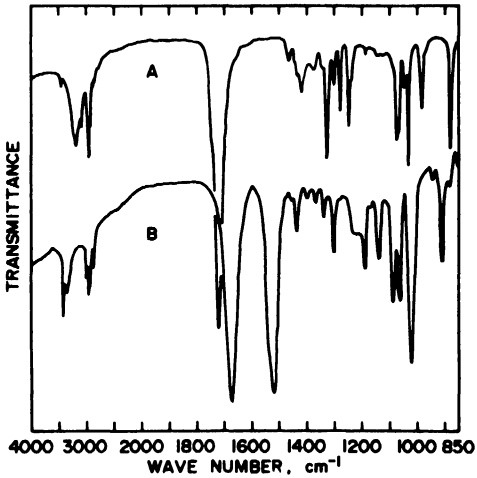


Fig. 1. Infrared spectra of 8-oxa-6-azabicyclo[3.2.1]octan-7-one (A, in carbon tetrachloride) and its polymer (B, in chloroform).

Anal. Calcd. for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.01. Found: C, 56.28; H, 7.19; N, 10.99%.

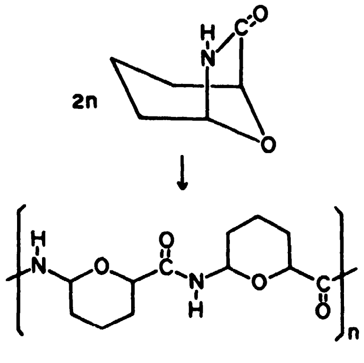
It should be noted that a driving force of this cyclization reaction may come from the activation of olefinic double bond induced by neighboring oxygen atom.

By means of conventional acylation method (11) N-acetyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one (V) was prepared from II, yield 62%; b.p. 85.5° (2 mm); infrared (CCl_4) 2940, 2860, 1758,and 1700 (νC=O), 1460, 1430, 1372, 1351, 1322, 1302, 1275, 1265, 1220, 1154, 1110, 1063, 1026, 980, 938, and 881 cm^{-1}; NMR (CCl_4) τ 8.18 (6H, $-CH_2-$), 7.52 (3H, $CH_3\overset{\overset{O}{\|}}{C}-$), 5.68 (1H, $-\overset{|}{C}H\overset{\overset{O}{\|}}{C}-$), and 4.21 (1H, $-O\overset{|}{C}H\overset{|}{N}-$); mass spectrum (m/e) 169 (M^+).

Anal. Calcd. for $C_8H_{11}NO_3$: N, 8.28. Found: N, 8.09%.

Anionic polymerization of 0.635g of II in 2 ml tetrahydrofuran was carried out in the presence of 20 mg of a 50% oil dispersion of sodium hydride and 0.01 ml of V in a nitrogen atmosphere for 1.5 hours. Even at 0°, II was easily polymerized to give polyamide (VI) in 52% yield, m.p. 234–238°, $\eta_{sp/c}$ 0.16 (m-cresol). At 100° bulk polymerization of II occurred as soon as the sodium hydride dispersion was added.

The infrared spectrum of resulting polyamide (VI) in chloroform (see Fig. 1) shows 3400 and 3350 (νNH), 3000, 2950, 2920, 2860, 1678 (νC=O), 1528 (δNH), 1440, 1400, 1370, 1340, 1307, 1193, 1145, 1092, 1068, 1030, 950, and 919 cm^{-1}. The nmr spectrum at 70° in deuterated chloroform presents a



VI

series of broad peaks centered at τ 8.15 (6H, $-CH_2-$), 5.95 (1H, $-\overset{|}{C}H\overset{\overset{O}{\|}}{C}-$), 4.8 (1H, $-O\overset{|}{C}H\overset{|}{N}-$), and 2.8 (1H, $-NH\overset{\overset{O}{\|}}{C}-$).

Further investigation of the optimum conditions for the synthesis of the new interesting bicyclic oxalactam and for the preparation of the new polyamide of much higher molecular weight and the polymer characterization are being carried out. Details of the research will be published in the near future.

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Received June 11, 1973
Revised July 31, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 639–643 (1973)

SOME ASPECTS OF THE POLYMERIZATION OF α-METHYL STYRENE AND N-VINYL PYRROLIDONE BY $AsCl_3$ AND $POCl_3$

In continuation of our work (1-3) on the polymerization of vinylmonomers by some Group V halides and oxyhalides, we have observed that $POCl_3$ is a more powerful initiating agent compared to $AsCl_3$ for the polymerization of monomers like α-methyl styrene and N-vinyl pyrrolidone. Some significant observations on these systems are reported here in this context.

The polymerizations of α-methyl styrene and N-vinyl pyrrolidone by $POCl_3$ were carried out at 25° in benzene and methylene chloride solvents respectively, and kinetic runs were performed using vacuum dilatometric techniques. Polymer molecular weights were determined cryoscopically in benzene.

TABLE I

Polymerization[a] of α-Methyl Styrene and N-Vinyl Pyrrolidone by $AsCl_3$

α-methyl styrene M	N-vinyl pyrrolidone M	$AsCl_3$ M	$[H_2O] \times 10^2$ M	% conversions at time in min		
				5	20	60
1	-	0.1	-	2	2	4
2	-	0.1	-	2	2	4
2[b]	-	0.2	-	2	3	4
2	-	0.1	1.4	2	3	4
2	-	0.1	2.3	2	3	5
2	-	0.1	3.3[c]	2	3	5
-	1	0.1	-	4	13	25
-	2	0.1	-	8	17	29

[a]These trial experiments were performed in benzene at 25°C under nitrogen atmosphere in pyrex reaction vessels (1-3).

[b]For the system α-methyl styrene (2M)–$POCl_3$ (0.2M)–benzene (25°C), the % conversions at 5 min, 20 min, and 60 min are 1,5 and 17 respectively (dilatometric readings).

[c]Represents the maximum concentration of water soluble in the reaction medium.

Table I convincingly demonstrates that $AsCl_3$ is indeed a poor initiator for the polymerization of α-methyl styrene. To test whether the polymerization is cocatalyzed by water, three sets of experiments were performed with varying water concentrations. Data of Table I clearly indicate the rate is not significantly improved in presence of water.

On the other hand, $AsCl_3$ at comparable concentrations ca., 0.1 M, can

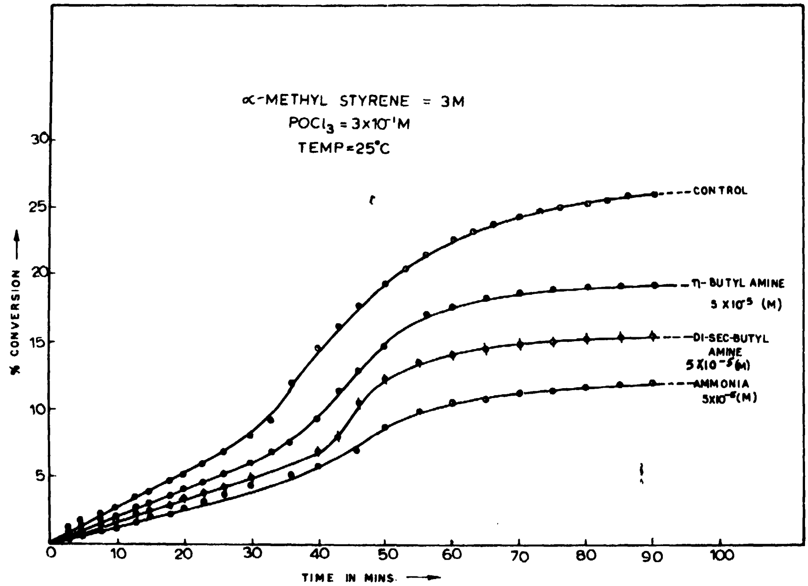

Fig. 1. Polymerization of α-methyl styrene by $POCl_3$ and effect of additives on the same: α-methyl styrene = 3 M; additives = as shown; temperature = 25°C; and $POCl_3$ = 3 X 10^{-1}M.

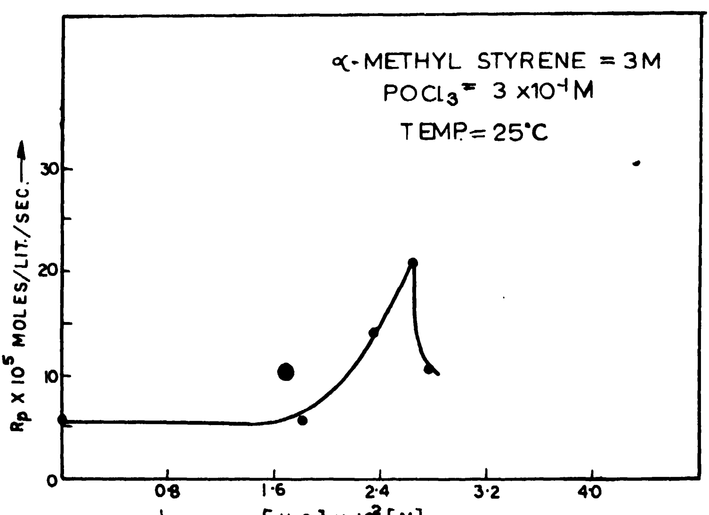

Fig. 2. Effect of water on the polymerization of α-methyl styrene: α-methyl styrene = 3 M; $POCl_3$ = 3 X 10^{-1}M; and temperature = 25°C.

satisfactorily initiate the polymerization of N-vinylpyrrolidone (Table I). These results, taken in conjunction with our previous observations (3) on $AsCl_3$,

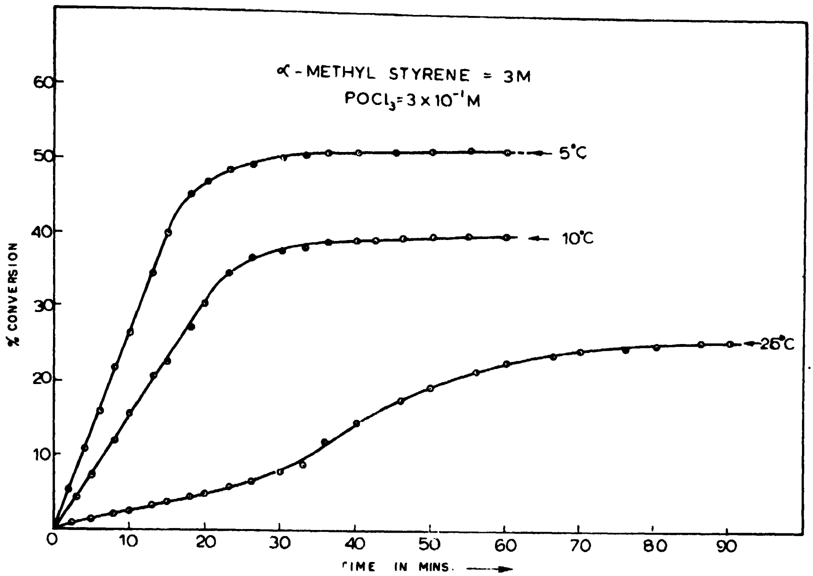

Fig. 3. Effect of temperature on the polymerization of α-methyl styrene by $POCl_3$: α-methyl styrene = 3 M; $POCl_3$ = 3 X 10^{-1} M; and temperature = 5°C, 10°C, 25°C.

initiated polymerization of N-vinyl carbazole and copolymerization of the same with styrene (2,3), clearly bring out the interesting feature that $AsCl_3$ is an efficient initiator for the polymerization of the N-substituted vinyl monomers.

$POCl_3$ has been found to be a more powerful initiator for the polymerization of these monomers. Percent conversion versus time data for α-methyl styrene (2M)–$POCl_3$ (0.2 M)–benzene system are presented in Table I. A comparison of these figures with those for α-methyl styrene (2M)–$AsCl_3$ (0.2 M)–benzene system amply justifies the above contention.* The polymerization characteristics of the system α-methyl styrene–$POCl_3$–benzene have been examined at several concentrations of the monomer and initiator respectively. A typical yield-time plot, obtained dilatometrically, for the system is shown in Figure 1. R_p, the rate of polymerization, has been found to be first order with respect to both $POCl_3$ and also the monomer. Figure 2 clearly indicates that the polymerization is cocatalyzed by water and that there is an optimum concentration of water where the rate attains a maximum. The polymerization is retarded by basic additives (Figure 1) including ammonia, n-butylamine and di-sec-butylamine (3). Figure 3 demonstrates that the polymerization is significantly accelerated by a decrease of temperature and the overall

*$POCl_3$, in as low as 10^{-3}M concentration successfully initiates N-vinyl pyrrolidone polymerization, while $AsCl_3$ is effective at hundred times higher concentration for the same monomer concentration (1-2 M).

energy of activation, $\bar{E}_p$ and that for the degree of polymerization $\bar{E}_{DP}$ have been estimated to be -18 and -3.6 kcals/mole respectively (4). Moreover, we have also noted that as the temperature is decreased, the initiator exponent does not change from unity, while the monomer (α-methyl styrene) exponent changes from unity to about 2. Worsfold and Bywater (5) observed a similar variation of the monomer exponent with temperature in α-methyl styrene polymerization by BF_3 in ethylene dichloride solvent.

At 25°, the degree of polymerization ($\bar{P}_n$) stays substantially constant at ca. 9 at a fixed α-methyl styrene concentration of 2M, while the $POCl_3$ concentration varies from 0.2–0.5M. However, at a fixed $POCl_3$ concentration of 0.2M, $\bar{P}_n$ increases from 9 to 13 to 15 as the monomer concentration changes from 2M to 3M to 4M respectively.

$POCl_3$ is indeed more active in initiating the solution polymerization of N-vinyl pyrrolidone. We have noticed in fact, that at equimolar concentration (2M) of N-vinyl pyrrolidone and α-methyl styrene, the former polymerizes with an initial R_p of 7.0×10^{-5} moles/lit/sec at a $POCl_3$ concentration of 2×10^{-3}M, while the latter does so with an initial R_p of 2.9×10^{-5} moles/lit/sec at hundred times higher $POCl_3$ concentration, viz. 2×10^{-1} M. The polymerization of N-vinyl-pyrrolidone is, however, immeasurably fast at this higher concentration of $POCl_3$.

The aforementioned results are consistent with a cationic mechanism. As regards the greater reactivity of $POCl_3$ over $AsCl_3$, as observed in the present context, it may be pointed out that the oxyhalides can act as oxygen as well as halogen donors (6) and are appreciably better halide ion donors than the halides (6). However, these aspects are receiving closer attention and the results of our comprehensive study of the kinetics, mechanisms, and other features of these systems will be reported in due course.

The authors thank the Council of Scientific and Industrial Research, India for financial assistance to P. K. M.

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Revised July 5, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 645–649 (1973)

A NEW METHOD OF STUDYING THE STRUCTURE OF BLOCK COPOLYMERS IN SOLUTION

We would like to show in this paper that the joint study of two component copolymers in dilute solutions by light, neutron, and X-ray scattering can give new information on the structure of such molecules that are inaccessible to each method separately. The suggested approach is based on the fact that the physical nature of scattering of the three above-mentioned types of emission is substantially different: X-ray scattering takes place on "free" electrons, light scattering occurs on "bound" electrons and neutrons scatter on nuclei. Therefore the "scattering capability" of a unit volume of the substance $\Delta\rho_i$ is stipulated by the electronic density in the case of X-rays, by the scattering length for neutrons and by the refractive index for light.

Indeed, let us consider a system consisting of two components with electronic densities ρ_1 and ρ_2, and, correspondingly, with volumes of V_1 and V_2. Let R_g be the electronic radius of gyration of all the system which can be determined by small-angle X-ray scattering, and R_1 and R_2 be the own electronic radii of gyration of the first and second components. If the system be immersed in a solvent with an electronic ρ_0 density, it is evident that

$$R_g^2 = \frac{\Delta\rho_1 \int_{V_1} (\vec{r})^2 \, dV_1 + \Delta\rho_2 \int_{V_2} (\vec{r})^2 \, dV_2}{V_1 \, \Delta\rho_1 + V_2 \, \Delta\rho_2} \tag{1}$$

where $\vec{r}$ is the vector drawn from the center of gyration of the system to any of its point, $\Delta\rho_1 = \rho_1 - \rho_0$, $\Delta\rho_2 = \rho_2 - \rho_0$. Let $\vec{r}_{01}$ ($\vec{r}_{02}$) be the vector drawn from the center of gyration of the system to the center of gyration of the 1st (2nd) component, and $\vec{r}_1$ ($\vec{r}_2$) the vector drawn from the center of gyration of the 1st (2nd) component to any of its point. Then

$$R_g^2 = \frac{1}{V_1 \, \Delta\rho_1 + V_2 \, \Delta\rho_2} \left[\Delta\rho_1 \int_{V_1} (\vec{r}_{01} + \vec{r}_1)^2 \, dV_1 + \Delta\rho_2 \int_{V_2} (\vec{r}_{02} + \vec{r}_2)^2 \, dV_2\right] =$$

$$= \frac{1}{V_1 \, \Delta\rho_1 + V_2 \, \Delta\rho_2} \left[\Delta\rho_1 V_1 R_1^2 + \Delta\rho_1 V_1 (\vec{r}_{01})^2 + \Delta\rho_2 V_2 R_2^2 + \Delta\rho_2 V_2 (\vec{r}_{02})^2\right], \tag{2}$$

inasmuch as from the definition of $\vec{r}_i$

$$V_i R_i = \int_{V_i} (\vec{r})^2 \, dV_i \quad \text{and} \quad 2\,\vec{r}_{0i}\, \Delta\rho_i \int_{V_i} r_i dV_i = 0.$$

It can be easily seen that in the case of a two-component system the vector $\vec{r}_{01}$ and $\vec{r}_{02}$ lie on one line and are opposite in sign, thus if $|\vec{r}_{01}| + |\vec{r}_{02}| = L$, then

$$\Delta\rho_1 V_1 |\vec{r}_{01}| = \Delta\rho_2 V_2 (L - |\vec{r}_0|) \tag{3}$$

In substituting (3) in (2) we have

$$R_g^2 = x_1 R_1^2 + (1 - x_1) R_2^2 + x_1 (1 - x_1) L^2, \tag{4}$$

where

$$x_1 = \frac{\Delta\rho_1 V_1}{\Delta\rho_1 V_1 + \Delta\rho_2 V_2} \tag{5}$$

is the relative "scattering capability" of the first component.

Formula (4) will also be valid for neutron scattering of the same two-component system, however ρ_1, ρ_2 and ρ_0 in this case should be understood as the average scattering length per unit volume determined as

$$\rho_i^{neutr.} = \frac{N_0}{M_i\bar{v}_i} \sum_k a_k b_k \tag{6}$$

(N_0 is Avogadro's number, M_i the molecular weight of the component, $\bar{v}_i$ its partial specific volume, b_k the scattering length of the k^{th} nucleus, and a_k is the number of such nuclei in the component).

It has been shown in a paper (1) that the radius of gyration R_g measured for two-component particles by light scattering also obeys the formula (4) in which

$$x_1 = \frac{C_1(dn/dc)_1}{C_1(dn/dc)_1 + C_2(dn/dc)_2} \tag{7}$$

Here C_1, C_2 are weight concentrations of the 1st and 2nd components, $(dn/dc)_1$ and $(dn/dc)_2$ are their refractive index increments.

From a comparison of formulae (5) and (7) it is easily seen that the role of $\Delta\rho_i$ in light scattering is played by the value

$$\Delta\rho_i^{light} = \frac{1}{\bar{v}_i} (dn/dc)_i \tag{8a}$$

or taking into account the Gladstone-Daly rule (see, for example (2))

$$\Delta\rho_i^{light} = (n_i^* - n_0), \tag{8b}$$

where n_i^*, n_0 is the refractive index value of the i-component of the solute and the solvent, correspondingly.

If the studied particle is a single component-one, the angle dependence of its scattering intensity (and, consequently, the experimental radius of gyration

R_g) will not depend on the nature of emission, though the intensities themselves can differ by several orders. At the same time the angle dependence of the scattering intensity for a two-component particle will be determined by the mutual arrangement of components as well as by their relative "scattering capability" which depends on the nature of the utilized emission.

For each emission taken separately the values $\Delta\rho_1$, $\Delta\rho_2$ and consequently x_1 can be different for different types of emission. It follows that having determined the experimental value R_g for each type of emission, it is possible to solve the system of formula (4) and to calculate the values R_1, R_2 and L which characterize the mutual arrangement of the components within the particle. Of course, variations of x_1 can also be attained within the framework of one type of emission by changing the solvent. However it is evident that the structure of the copolymer can change due to a change of the thermodynamics of the polymer-solvent interaction.

As an example we shall calculate the values x for the copolymer styrene–methylmethacrylate in dioxane and benzene[a]. Values of "scattering capabilities" of the unit volume $\Delta\rho_i$ for neutron scattering were calculated by formula (6), and for X-ray scattering by the formula

$$\rho_i^{\text{X-ray}} = \frac{A_i}{M_i} \frac{N_0}{\bar{v}_i} \tag{9}$$

where A_i is the number of electrons in the component. The values $\bar{v}_i$ were taken from the paper (3) t° = 25°C: 0.927 ml/g and 0.917 ml/g for polystyrene (PS) in dioxane and benzene and 0.818 ml/g and 0.807/ml/g for polymethylmethacrylate (PMMA) in the same solvents. At calculation of the values of neutron scattering, standard values of scattering length of nuclei were taken: +6.61, +5.80 and $-3.67 \cdot 10^{+10}$ cm/cm^3 correspondingly for C, O, H (see, for example, (4)). The refractive index increments dn/dc are taken from the paper (3): (all the values are for λ = 4360 Å), PS in dioxane = +0.185 ml/g, PS in benzene +0.110 ml/g, PMMA in dioxane +0.072 ml/g and PMMA in benzene = 0.00 ml/g. The $\Delta\rho_i$ values calculated from these data are given in Table 1. The x_1 values are calculated for the styrene component according to formula (5) the dependence of which on the PS volume fraction in the copolymer in the two solvents is presented in Figure 1.

As seen in Figure 1, the x_1 value of this component changes within the limits sufficient for a reliable determination of the values R_1, R_2 and L for the three described types of emission within the large interval of the polystyrene volume fraction.

Thus, if we proceed from a 2% error in determining the R_g values for all the three methods, the error in determining R_{PS} and R_{PMMA} will be ± 6 Å and ± 8 Å for L for the hypothetic PS–PMMA block copolymer with polysty-

[a]The application of the suggested method for some two-component biological macromolecules will be presented in another publication.

TABLE I

Scattering Capabilities of the Unit Volume of the Substance $\Delta\rho$ for Different Types of Emission for PS and PMMA in Dioxane and Benzene

Solvent	Polymer	X-rays in $e/\text{Å}^3$	Neutrons in $cm/cm^3 \cdot 10^{-10}$	Light $\lambda_0 = 4360$ Å
Dioxane	PS	0.011	+0.34	0.200
	PMMA	0.056	+0.75	0.088
Benzene	PS	0.067	+0.29	0.122
	PMMA	0.113	+0.20	0

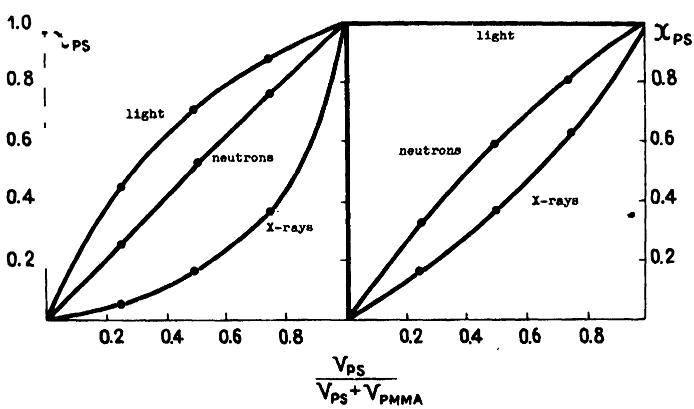

Fig. 1. Dependence of the relative "scattering capability" of polystyrene X_{PS} on its volume fraction for the copolymer PS–PMMA in dioxane (to the left) and in benzene (to the right).

rene in a 0.5 volume fraction in dioxane with $R_{PS} = R_{PMMA} = 80$ Å and L = 200 Å. In the case of the same copolymer in benzene the precision of R_{PS}, R_{PMMA} and L determination will be better owing to the fact that one of the methods (light scattering) "sees" only the styrene component. And, finally, for the block copolymer PS–PMMA–PS when L is close to zero, the error in determination of R_{PS} and R_{PMMA} will only insignificantly exceed the experimental error in R_g determination. These evaluations, as well as general consid-

erations, show that the suggested method of studying copolymer structure can be particularly interesting for block copolymers as it allows to not only control the chemical structure of the copolymer, but also to quantitatively observe the behavior of each block separately at a change of medium conditions.

In conclusion it should be noted that using X-ray small angle scattering the radii of gyration of statistical coils can already be measured (5,6), while neutron small angle scattering on solutions is not yet well enough developed and the light scattering method is traditionally used for determination of the radii of gyration of particles larger than 200 Å. However, progress in development of neutron scattering (7,8), as well as direct proof of the possibility of applying the light scattering method for evaluation of particle size in the 70–200 Å interval (9,10) give assurance that the complex utilization of the three analyzed methods will become possible in the nearest future.

The authors thank Professor O. B. Ptitsyn for reading the manuscript.

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ACID CATALYZED GRAFTING OF MONOMERS TO WOOL

We have found that certain mineral acids rapidly catalyze the graft polymerization of styrene and other monomers to wool in the presence of a swelling solvent. It has recently been shown that using an aqueous emulsion system, ethyl acrylate grafts "spontaneously" to wool in the presence of a swelling solvent, a long induction period being observed (1). In the present work, no induction period (Fig. 1) is found even with ethyl acrylate (2), but the grafting reaction becomes extremely rapid after a certain level of copolymerization has been attained (Table I). It is probable that this change in rate coincides with a change from a diffusion controlled reaction to one which is essentially a bulk reaction, and may correlate with the breaking up of the scalar outer casing of the wool fiber. This type of rupture would be consistent with the mechanochemistry technique of grafting discussed by Stannett and coworkers (3). Current experiments are being designed in an attempt to obtain photomicrographic evidence to confirm this theory.

The experimental technique consists of reacting the wool sample with a solution of, typically, styrene in methanol containing catalytic amounts of mineral acid for various times at the required temperature. Air appears to exert

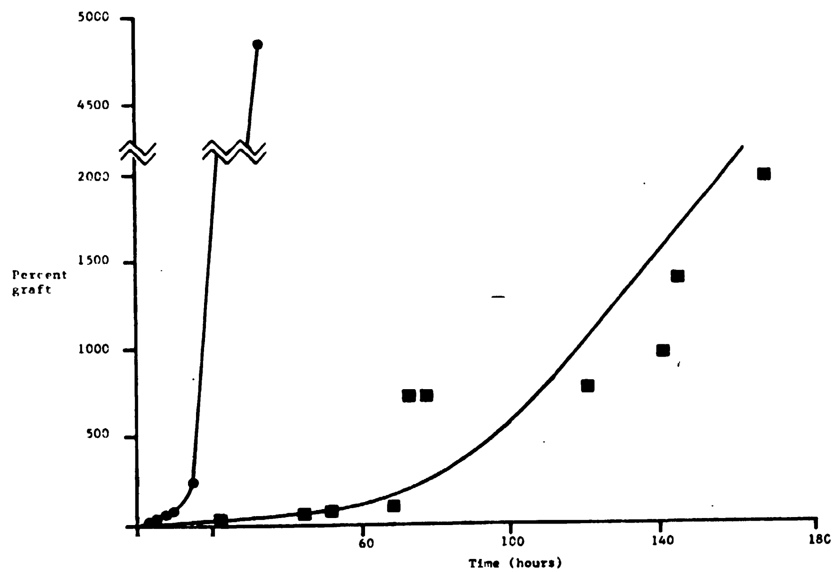

Fig. 1. Grafting of styrene to wool cloth in methanol solution, 0.2N in HNO_3; ● 75 percent styrene at 43°C; ■ 75 percent styrene at 23°C.

TABLE I

Grafting of Styrene to Wool in Methanol Solution[a]

23°				43°			
50% Styrene		75% Styrene		50% Styrene		75% Styrene	
Time (hrs)	% Graft[b]	Time (hrs)	% Graft[b]	Time (hrs)	% Graft[b]	Time (hrs)	% Graft[b]
72	9.3	6	6.8	0.5	2.9	1	5.7
96	18	22	17	1.0	4.0	2	12
120	15	44	57	1.5	4.6	3	20
144	10	51	64	2.0	7.5	4	27
168	12	68	93	3.0	12	5	35
240	7.6	72	735	4.2	23	6	40
264	9.1	77	722	5.0	26	7	45
312	11	96	1270	6.0	33	8	56
312	10	120	775	7.0	41	9	69
336	22	140	970	8.3	46	14	242
		144	1405	9.3	51	32.5	4850
		168	1990	10.1	44		
				24	51		
				72	68		

[a]An effectively "infinite" liquor to wool ratio was used in these runs; solution 0.2 N in HNO_3.

[b]% Graft calculated as the % increase in weight of the dry wool.

negligible effect on the reaction. The physical form of the wool affects the grafting rate, loose wool fibers (wool top), and wool powder grafting more rapidly than wool cloth. Very highly grafted fibers increase their physical dimensions several times, and eventually stretch apart (> 5000% graft). Extremely slow grafting is observed over long periods in the absence of acid.

The grafting rate is increased remarkably by increasing the monomer concentration (Fig. 2) or the temperature (Table I). The grafting rate is very slow at 2°, but becomes significant at 23°, and very fast at 43°. The runs are more reproducible at 43° than at 23° (see poor correlation of graft versus time at 23°, Table I) but no reason for the erratic behaviour at the lower temperature is apparent.

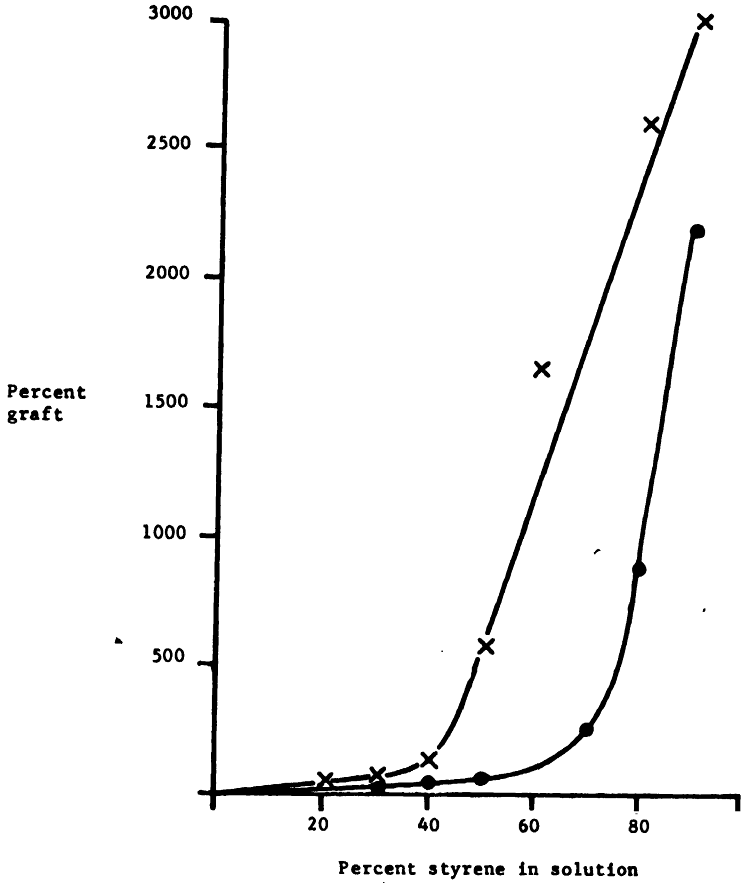

Fig. 2. Typical variations of percent graft of styrene to wool cloth with variation of styrene concentration in methanol; X, Solutions 0.2N in HNO_3, reacted 240 hours at 23°C; ●, Solutions 0.2N in H_2SO_4, reacted 45 hours at 50°C.

Experiments indicate that polymerization of monomer occurs predominantly within the wool structure and not in the bulk solution. The acid catalyzed reaction is eliminated by conventional free radical inhibitors. Other solvents which are effective in the reaction in addition to methanol include dimethylsulphoxide, dimethylformamide, and ethanol. Of the successful mineral acids used as catalysts, sulfuric and nitric acids are the most efficient. Styrene has been used as typical monomer in the examples cited (Figs. 1 and 2, Table I) since highest grafts have been obtained with this monomer. Other monomers have also been copolymerized (less efficiently) to wool with this acid technique (2). The procedure is also attractive for comonomer work, especially if styrene is one of the monomers used (2). Full details of these related experiments will be published elsewhere.

We thank the Australian Institute of Nuclear Science and Engineering and the Australian Atomic Energy Commission for the irradiations. We are also grateful to the Australian Research Grants Committee and the Australian Wool Corporation for continued support.

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BOOK REVIEWS

The Physics of Glassy Polymers, R. N. Haward, Ed., Halsted Press, New York, 1973. 620 pp. $45.00.

The book is extremely timely, reviewing a field which is of so much theoretical and practical importance. The editor was able to get excellent coworkers who treated their own fields very well. Most chapters not only introduce the field to the beginner, but also bring advanced results and conclusions valuable to the expert worker in the field. The editor succeeded in avoiding serious overlaps and to some extent also the too personal bias of contributions. As is always the case with so many contributors, the level of treatment differs more from one contribution to the next than the average reader would like. But this is not a serious criticism because the book as a whole is excellent.

The single chapters treat:

The Thermodynamics of the Glassy State
X-Ray Diffraction Studies of the Structure of Amorphous Polymers
Relaxation Processes in Amorphous Polymers
Creep in Glassy Polymers
The Yield Behaviour of Glassy Polymers
The Post-Yield Behaviour of Amorphous Plastics
Cracking and Crazing in Polymeric Glasses
Rubber Reinforced Thermoplastics
The Diffusion and Sorption of Gases and Vapors in Glassy Polymers
The Morphology of Regular Block Copolymers

The referee would like to have an additional chapter on glassy state of the amorphous components in crystalline polymers. But this would very likely demand an expansion of the scope of the book in a direction which is not yet sufficiently understood and is therefore less suitable for a comprehensive treatment.

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Received July 25, 1973

Organoaluminum Compounds, T. Mole and E. A. Jeffery, Elsevier Publishing Co., New York, 1972. 465 + XIV pp. $61.75

Prodigious amounts of chemical research and development work has been done in the field of organoaluminum chemistry, particularly since the commercialization about fifteen years ago of Ziegler-Natta polymerizations employing diverse organoaluminum compounds. The time has indeed come for an organized summary and critical survey of this huge field. The authors have partially fulfilled this task: they have collected, abstracted, and excellently organized a vast amount of published material (all significant contributions to the scientific literature of organoaluminum chemistry have been considered up to late 1971); however, they failed to criticize and evaluate the available information. Their exciting subject did not become alive with personal comments, observations, conclusions.

The book is first of all for organometallic chemists, then for organic chemists interested in organic reaction of aluminum, and then to a much lesser degree for polymer chemists. The book starts with a brief Introduction (6 pp.) and continues with chapters on Organoaluminum Halides (~40 pp.), Organoaluminum Hydrides (~30 pp.), Trialkylaluminums (~40 pp.), Reactions of Trialkylaluminums with Olefins (~20 pp.), and Arylaluminums (~15 pp.). Preparation and properties of these compound classes are emphasized. The next five chapters concern more complicated compounds: Organoaluminates (~30 pp.), Organoaluminum Alkoxides and Related Compounds (~20 pp.), Organoaluminum Amides and Related Compounds (~20 pp.), Sulphur, Phosphorous and Arsenic Compounds (~10 pp.), and Unsaturated Organoaluminum Compounds (~25 pp.). The rest of the chapters deal with various reactions: Reactions with Unsaturated Oxygen, Nitrogen and Sulphur-containing Functional Groups (~50 pp.), Reactions with Organic Halides, Ethers and Polar Monomers (~20 pp.), Alkylation of Compounds of the Non-transition Elements (~20 pp.), and Reactions with Compounds of the Transition Metals (~30 pp.). The last chapter is a brief Analysis of Organoaluminum Compounds (~4 pp.). The book ends with a most useful Index of Organoaluminum Compounds, which lists some 350 different species and refers to the text for details, and a good General Index.

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Gel Permeation Chromatography, Jack Cazes, American Chemical Society Audio Courses, 4 cassettes plus 205 pp. $45

This was the reviewer's first experience with an audio course, and it was a welcome change from "plowing" through a book. The set includes four cassettes (a total of 222 min of lecture) and a course manual (205 pp.). This course is a direct audio version of Cazes' ACS Short Course on gel permeation chromatography (GPC).

The audio was very good, and the lecturer's voice was distinct and easy to listen to, all a must for the "reader" to obtain full comprehension from the course. The manual was easy to read and follow during the course. It is strongly recommended that each listener have his own manual (extra manuals are available from the ACS), because one will probably add one's own "notes" as the course proceeds.

The course covers all of the important aspects of GPC including instrumentation, the separation process, calibration of GPC systems, molecular weight distribution calculations, quantitative analysis, preparative-scale GPC, and fractionation of low molecular weight substances (nonpolymers). An especially strong point of the course is the chapter on GPC of low molecular weight substances (below 1000 mol. wt.). Often, chemists think of GPC only in terms of its ability to give molecular weight distributions of high polymers. In Cazes' chapter on low molecular weight substances, he stresses the utility of GPC for these applications and helps the reader "around some not-so-obvious pitfalls" in terms of chromatogram interpretation and calibration.

Some of the illustrations in the manual were good, notably A10, A11, B10A, and M28. A novice to GPC will probably find it necessary to go through p. 53-56 on GPC calibration several times to understand completely all the necessary steps in constructing and interpreting the different calibration methods. In later versions of this manual, the inclusion of a general listing of terms and definitions in the introduction section might be helpful.

The manual includes a comprehensive 7-page bibliography which will be helpful to the novice and to the experienced user when faced with a new application. In addition, there is a good manual index, and the contents page lists those sections of the manual which are covered on each side of the tapes. This is a great aid when going back and reviewing a particular section. The feature of an audio course which allows one to "hear" certain sections again and at one's own pace might recommend this version over the "live" course.

The course will prove to be useful to novices as well as experienced chromatographers. (A quick half-dozen telephone calls to other chemists completing this course confirmed this reviewer's feelings.) The price of the course will probably prohibit the purchase by individuals, but chemical libraries will find the waiting list for this course long, and duplicate copies may be necessary.

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Received June 4, 1973

Chemical Modification of Papermaking Fibers, Kyle Ward, Jr., Marcel Dekker, Inc., New York, 1973. 246 pp. $18.50

This book is concerned with chemical modifications of papermaking fibers. It consists of chapters devoted to the following types of chemical changes which have been used or tried in efforts to produce new or improved properties in paper products: esterification, etherification, oxidation, crosslinking, and graft polymerization. The author refers to his book as a "review", and he has made a great effort to make the record as complete as possible on references in each of these five subject areas. Partly because of the different degrees of success researchers have had in applying the different modification techniques, and partly as a reflection of his own interests, the author's treatment of these five areas is not very even. The chapter on oxidation consists of thirteen pages without tables or illustrations, whereas the chapter on etherification, an area in which the author has done considerable work, consists of 70 pages including 28 figures and 8 tables.

The unevenness of treatment occurs throughout the book. At times good explanations are given for the mechanisms of chemical action as, for example, in the discussion on urea formaldehyde resins as wet-strength agents for paper, and the explanations of reactions involved with grafting atents such as Fenton's reagent. On the other hand, often no details are given in broad areas, and the reader is merely referred to other review papers. Such examples occur on pages 116, 118, 134, 168, and 184 and refer to areas such as yellowing, wet-strength papers, and cellulose graft polymers.

An important shortcoming of this book, in this reviewer's opinion, is the lack of critical evaluation of contributions in many fields. An example of this occurs on page 182 where the author states that, "Grafting is in the amorphous regions of the pulp." In the discussion of this concept, it is evident that the author still accepts uncritically the assumption that the cellulose microfibrils in pulp fibers have crystalline and amorphous regions, a concept that has been under heavy challenge for at least ten years in the scientific literature. Since little or no critical evaluation is made of the multitudinous references in the book, the reader must separate the dross from the ore himself in bridging "the gap between research and industrial applications."

This reviewer must mention several other deficiencies that make this book something less than a great buy at $18.50. There are some errors. In the chapter on crosslinking, the author equates embrittlement with weakness, a layman's concept. Technically, brittle is not the reverse of strong, but rather the reverse of ductile. High carbon steel, a rather strong metal, is relatively brittle in that it undergoes very little nonlinear elongation before fracture. There are some sweeping generalities as, for example, "The effect of chlorine at acid or alkaline pH is small," a statement relative to the effect of oxidation on wet strength. The reader must examine the subsequent paragraphs carefully to find the basis for this broad statement; it turns out to be based on three specific types of treatment: acid chlorite, sodium borohydride, and hydroxylamine.

Aside from these and a few other technical points, the work has one writing flaw that makes it more difficult to use than it should be. The author's style is difficult in that he has a habit of making paragraphs where they should not exist. Examples such as these will illustrate the point. These are all first sentences of paragraphs:

> "Yoshino and co-workers found that nitrogen dioxide, as well as periodiate, oxidation has this effect on strength." (p. 119)
> "It has proved a useful criterion for choosing possible new crease-proofing agents in the textile industry." (p. 132)
> "In one paper they describe a condensation-type graft polymer, using difunctional isocyanates and dihydroxyl compounds." (p. 208)

In places such as these, the reader is forced to read back into the preceding paragraph or sometimes further to decide who or what the author is talking about. There are other places where the author starts a subject and describes some work in one paragraph but does not get around to providing the reference until some subsequent paragraph. The fault here lies principally with the editorial staff of the publisher; many good technical people are not gifted with the faculty for writing clearly and must rely upon the publisher to assist them in this regard. If one considers this inadequate editorial assistance together with the fact that the manuscript is typewritten, the quality of the book suffers in comparison with other technical works in the same price range. Fortunately, the typing itself was done very accurately.

For those who require a tying together of the patent and industrial literature with research on chemical modification, this book will be a useful source. Its other uses, particularly for teaching, would be limited.

R. E. Mark

ESPRI
Syracuse, New York

Received February 1, 1973

ANNOUNCEMENTS

7th Symposium on Plastics Processing in the IKV/Aachen

The 7th Symposium on Plastics Processing will be held by the Institute for Plastics Processing, from March 20th to March 22nd, 1974 at Aachen, Germany.

For further information, write to the Institute Director, Prof. Dr.-Ing. G. Menges, Institut für Kunststoffverarbeitung, 51 Aachen, Pontstr. 49, Germany.

Polymer Symposium at MMI (MMM 3)

Midland Macromolecular Institute (MMI) will sponsor an international symposium on "Polymerization in Ordered Systems" to be held in Midland, August 19-23, 1974. The symposium will consist of both invited and contributed papers. The invited papers will offer critical reviews on polymerization of micelles, mesophases, mono- and multilayers, and monomer crystals. Contributed papers are solicited. For further information write: Symposium Secretary, Midland Macromolecular Institute, 1910 West St. Andrews Drive, Midland, Mich. 48640, USA; Telephone (517) 631-9450.

Polymer Symposium at MMI (MMM 4)

Midland Macromolecular Institute (MMI) will sponsor an international symposium on "Molecular Transitions and Relaxations" in honor of Dr. Raymond F. Boyer to be held in Midland, Mich., February 6-7, 1975. The symposium will consist of 8-9 invited papers which will offer critical reviews on phenomena and methods, motions in liquid crystals, crystalline and amorphous polymers, and in low molecular weight fluids and glasses, definitive subgroup motions, structure/property relationships, and on interpretations of motions in selected polymers. For further information write: Symposium Secretary, Midland Macromolecular Institute, 1910 West St. Andrews Drive, Midland, Mich. 48640, USA; Telephone (517) 631-9450.

Congratulations to Professor Otto Wichterle

Polymer scientists throughout the world are glad to congratulate Professor Otto Wichterle on his sixtieth birthday anniversary, 27 October, 1973.

He has made unique advances in macromolecular chemistry which have had big scientific and industrial significance. We all remember the international conferences he organized in Prague in 1957 and 1965. The reputation of the Institute of Macromolecular Chemistry, Prague, founded by him is considerable and world wide.

The International Union of Pure and Applied Chemistry and all scientific workers in the field of macromolecules owe a great debt to him for his leadership in the creation of the Macromolecular Division of the Union, covering all aspects of the science of macromolecules. This occurred in the 1967 Conference of the Union in Prague. Under his leadership as first president the Division worked with considerable success to bring about collaboration in macromolecular science between chemist and physicist, pure and applied workers, university and industry all over the world.

For these and many other contributions to the world of science, we thank Professor Wichterle and convey to him our respect and best wishes.

Symposium on Fiber and Textile Science and Engineering

This symposium is sponsored by the East Tennessee Section of the American Chemical Society and the College of Engineering, The University of Tennessee, Knoxville, Tennessee 37916, and will be held on Monday and Tuesday, November 12-13, 1973, at The University of Tennessee, Knoxville, Tennessee.

The program consists of the following:

Session I. "Polymer Processing and Fiber Spinning," J. L. White, Chairman. 9:00 A.M. Monday, November 12.

Session II. "Polymerization and Polymer Modification," J. F. Fellers, Chairman. 2:00 P.M., Monday, November 12.

Session III. "Novel Fibers: Structure-Property Relationships," E. S. Clark, Chairman. 9:00 A.M., Tuesday, November 13.

Session IV. "Fire Retardants and Fabric Flammability," M. E. Carter, Chairman. 2:00 P.M., Tuesday, November 13.

For further information, contact Professor J. L. White, Department of Chemical and Metallurgical Engineering, The University of Tennessee, 615–974-2577.

Call for Abstracts

Brief contributed papers emphasizing the characterization and utilization of materials in problems relating to the energy crisis are being solicited for our 14th Annual Symposium. This symposium, jointly sponsored by American Society of Mechanical Engineers, American Society of Metals, and the University of New Mexico will be held February 28–March 1, 1974, at the Hilton Inn in Albuquerque, New Mexico. Every effort will be made to accommodate all contributors and accepted abstracts will be published in the Symposium Proceedings. One page abstracts should be sent before January 15, 1974 to: F. P. Gerstle, Jr., Organization 5314, Sandia Laboratories, Albuquerque, N. M. 87115, or Olden J. Burchett, Organization 1541, Sandia Laboratories, Albuquerque, N. M. 87115.

ERRATUM

EFFECT OF SUPPORTING ELECTROLYTE ON THE ELECTROINITIATED POLYMERIZATION OF ACRYLONITRILE

KANJI SATO, MASAAKI OGASAWARA, and KOICHIRO HAYASHI
Faculty of Engineering, Hokkaido University, Sapporo, Japan

(article in J. Polymer Sci., Polymer Letters Edition, 11, 5 (1973))

On page 10, the R_p values in Table II should read as follows:

Supporting electrolyte	$R_p \times 10^4$, mol/liter·sec
$(CH_3)_4NClO_4$	0.67
$(C_2H_5)_4NClO_4$	0.82
$(n{-}C_3H_7)_4NClO_4$	1.29

On lines 17 and 18 of page 12, "1570cm^{-1} assigned to –C=N–." should read "1670cm^{-1} assigned to C=N."

The *Journal of Polymer Science* publishes results of fundamental research in all areas of high polymer chemistry and physics. The *Journal* is selective in accepting contributions on the basis of merit and originality. It is not intended as a repository for unevaluated data. Preference is given to contributions that offer new or more comprehensive concepts, interpretations, experimental approaches, and results.

In addition to meeting these standards for excellence and significance, manuscripts for the *Polymer Letters Edition* must exhibit a special degree of novelty and timeliness that warrants speedy publication, even in brief preliminary form. Short contributions that do not in the opinion of the editors meet this test, but are otherwise acceptable, will be published as *Notes* in the *Polymer Chemistry* or *Polymers Physics Editions.*

Three copies of every manuscript are required. They may be submitted to the appropriate editor: C. G. Overberger (chemistry, physical organic chemistry), Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, or T. G Fox (physics, physical chemistry), Mellon Institute, Pittsburgh, Pennsylvania 15213. Alternatively, manuscripts may be submitted through the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201. All other correspondence should be addressed to Periodicals Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016.

Detailed instructions on preparation of manuscripts are given frequently in the *Polymer Chemistry* and *Polymer Physics Editions.*

Polymer Letters Edition

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Journal of Polymer Science: Polymer Letters Edition

The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition*, monthly; *Polymer Physics Edition*, monthly; *Polymer Letters Edition*, monthly; *Polymer Symposia*, irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition*, *Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

POLYMER LETTERS EDITION VOL. 11, PP. 667–672 (1973)

A USEFUL VISCOSITY TEMPERATURE RELATION

Numerous equations for the dependence of the zero shear viscosity on temperature exist (1-5). To varying degrees, some of these relations date back to the earliest concepts of free volume invoked by Batschinski (1) and later by Vogel (2) and Fulcher (3). More recently, the free volume models have had considerable success via the work of Williams, Landel and Ferry (WLF) (4), and others (5-10). Some workers (11-14) have made other attempts to account for the temperature dependence of the viscosity from a more fundamental basis. In these equations, a ratio of viscosities is related to a difference of temperatures, whereas, here it is related to a temperature ratio.

In this note, we propose viscosity-temperature relation valid for a wide variety of materials, using a minimum number of adjustable parameters. This equation may be expressed as

$$\ln(\eta/\eta_s) = f\{(T - T_g)/(T_s - T_g)\} \tag{1}$$

i.e., the viscosity ratio, η/η_s, of diverse materials is as a universal function of $(T - T_g)/(T_s - T_g)$ where T_g is the glass transition temperature, and T_s is a reference temperature above T_g. The reference viscosity, η_s is the viscosity at T_s and η is the viscosity at T.

This model evolved as a result of our preliminary analysis of viscosity and crystal growth rate data of polymers (15), organic molecules, and inorganic high melting materials with low coordination numbers (16). At first, we found that the relation

$$\ln(\eta/\eta_m) = f\{(T - T_g)/T_m - T_g)\} \tag{2}$$

reduced the extensive viscosity data of 1:3:5 tri-α-naphthylbenzene (5) and 1:2 diphenylbenzene (6,17) to a single curve. Here η_m is the zero shear viscosity at the melting point, T_m. However, it is not as successful as eq. (1) when applied to a much larger number of materials. It was also realized that while the melting temperature is a useful reference point for correlating crystalline property (15,16), T_g or T_∞ (normally lying about 50°C below T_g) best describes the properties associated with the liquid-like nature of materials (7,8, 18).

From experimental data, it was in fact found that

$$T_s = T_g(1 + \phi) \tag{3}$$

where $\phi = 0.24$ for all materials gives a relatively good fit to the data. Hence, eq. (1) can be rewritten as

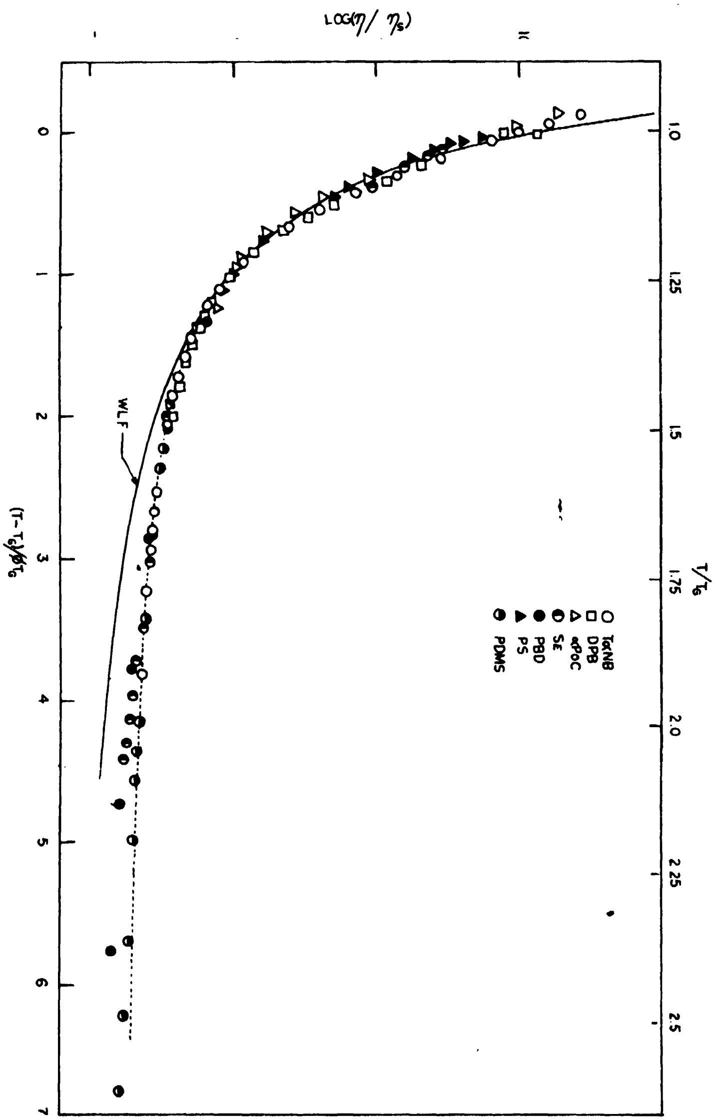

Fig. 1. The viscosity ratio η/η_s plotted as a function of reduced temperature function $(T - T_g)/\phi T_g$ (lower scale) and T/T_g (upper scale). η_s is the viscosity at temperature, $T_s = 1.24\ T_g$. The materials (with abbreviations) are: 1:3:5 tri-α-naphthylbenzene (TαNB), 1:2 diphenylbenzene (DPB), α-phenyl-o-cresol (α-P-o-C), selenium (Se), polybutadiene (PBD), polystyrene (PS), polydimethylsiloxane (PDMS). The dotted line is a plot of eq. (7). The solid line is a standard WLF plot with the same T_s. Temperatures are expressed in °K.

$$\ln (\eta/\eta_s) = f(T - T_g)/\phi T_g = g(T/T_g) \tag{4}$$

TABLE I

Parameters Used in Plotting Figure 1

Material	T_g (°C)	T_s (°C)	η_s (poises)	Reference
1:3:5 TαNB	69.2	151.2	19.06	(5)
1:2 DPB	-30.0	28.4	6.92	(6, 17)
α-φ-o-cresol	-53.0	-0.2	4.17	(17)
selenium	30.0	102.6	3.63×10^3	(20, 21)
poly(butadiene)	-95.0	-52.3	8.91×10^9	(8)
poly(styrene)	100.0	189.5	2.82×10^2	(8)
poly(dimethylsiloxane)	-123.2	-87.2	1.70×10^8	(8)

in terms of known experimental parameters where g is also a universal function. The ratio η/η_s is plotted in Figure 1, the ordinate is indicated as T/T_g on the top of the graph, and $(T - T_g)/\phi T_g$ at the bottom. Data for different materials are included. The values used for η_s, T_s and T_g are listed in Table I. From this graph, the viscosity-temperature dependence of any material can be deduced from a knowledge of its glass temperature and a single viscosity value, η, corresponding to a given temperature.

A variety of other equations can be written* for master curves relating a reduced viscosity with a function of reduced temperature variables. Equation (4) is presently preferred because it can describe a universal curve in terms of measurable properties. Furthermore, it represents experimental results over a very wide temperature range. It is worth noting that the master curve depicted in Figure 1 traverses the conventional glass temperature and covers more than 16 orders of magnitude in viscosity as well as a vast temperature span. For comparison purposes, a WLF type plot (solid line in Figure 1) was made with the same reference temperature T_s as in eq. (1) for the 1:3:5 TαNB data. The parameters were determined according to the procedure recommended by Ferry (19). It is clear from this plot that considering the entire viscosity-temperature range, a less satisfactory representation pertains when the WLF relation

*For example,

$$\ln(\eta/\eta_s) = f\{(T - T_\infty)/(T_s - T_\infty)\} = g'(T/T_\infty)$$

should also provide a master curve relating the viscosity ratio η/η_s with the temperature ratio T/T_∞. At the present stage of the analysis, the T_g correlation of eq. (4) is preferred because there is more uncertainty in the values of T_∞ than T_g. Here T_∞ is equivalent to T_2 in the Gibbs-DiMarzio notation (see reference (13)).

is used. Again, a detailed analysis of the 1:3:5 TαNB data given elsewhere (see Figures 2 and 15 of reference (5)) clearly indicates that representation of the experimental data by a single Vogel relation is inadequate. In fact, the viscosity data cannot be described by either two such relations or a Macedo-Litovitz composite equation (9). A wide selection of data and a wide range of viscosities have been analyzed (8) along conventional lines.

Following Berry and Fox (8) we define

$$\Delta = T_g - T_\infty$$

and, using eq. (3), we can rewrite the Vogel viscosity relation (2) as

$$\ln\left(\frac{\eta}{\eta_s}\right) = C\left[\frac{(1+\phi) - T/T_g}{(T/T_g + \Delta/T_g - 1)(\phi + \Delta/T_g)}\right] \tag{5}$$

Consistency with eq. (4) requires that Δ/T_g, C, and $T_s - T_g)/T_g$ be constants. Similarly, it can be shown that the W.L.F. eq. (4) becomes

$$\ln\left(\frac{\eta}{\eta_s}\right) = C_1\left[\frac{T/T_g - (1+\phi)}{C_2/T_g + T/T_g - (1+\phi)}\right] \tag{6}$$

where C_1, C_2/T_g and $\phi = (T_s - T_g)/T_g$ are required to be constants. A little further manipulation can convert the right-hand side of eq. (6) to that of eq. (5). The anticipated equivalence of the Vogel and W.L.F. relations is established if $C_1 = -C$. It is now clear from eq. (5) and (6) that each of these relations needs three universal constants to correlate viscosity with temperature, whereas in our relation η/η_s is a function of T/T_g alone.

An empirical equation which describes all the data in Figure 1 rather well is

$$\log(\eta/\eta_s) = A\left[\exp\{B\,T_g/T\} - \exp\{B/(1+\phi)\}\right] \tag{7}$$

where A = 0.0111 and B = 7.19 (see dotted line). At low temperatures this curve coincides with the WLF equation.

The viscosities, calculated from eq. (7), are in good agreement with experimental results for 1:3:5 TαNB as can be seen from Table II which lists some typical values for this material. Deviations are greatest at the high viscosity end where the curve of η superimposes the WLF range. Perhaps a better, or even an individual value for ϕ and hence T_s may be needed for each substance. Deviations from our chosen value of ϕ may be responsible for some of the observed scatter in Figure 1. Our present correlation, eq. (7), fits all the experimental data in Figure 1 within about a factor of 2 in η. Considering the extensive temperature and viscosity range covered, this is better than other models so far proposed. It is pertinent to indicate that much of the viscosity-temperature data in the literature covers a limited range, so that an accurate assessment of η_s is not always possible. Further refinement of the values in Table I may lead to a better correlation.

TABLE II

Viscosity Temperature Data for 1:3:5 TαNB

Temperature °C	T/T_g	Experimental $\log \eta/\eta_s$	Calculated $\log \eta/\eta_s$
79.2	1.029	8.18	8.40
99.2	1.088	4.97	4.59
144.3	1.219	0.37	0.39
160.0	1.265	-0.47	-0.40
189.0	1.358	-1.54	-1.46
210.0	1.411	-1.85	-1.86
277.0	1.607	-2.64	-2.70
310.6	1.705	-2.84	-2.92
357.5	1.842	-3.08	-3.12
407.0	1.987	-3.27	-3.26

From the results and formulations presented in this article, it is demonstrated that a useful relation between viscosity and temperature is expressed in terms of this parameter T/T_g or $(T - T_g)/\phi T_g$ rather than $(T - T_g)$, is warranted for a variety of different classes of materials. This new approach seems to have sufficient value to merit further investigation. The relation presented here should also be applicable to diffusion, creep behavior, and other materials parameters commonly fitted by WLF type equations.

A more detailed manuscript on this relation is in preparation.

We are grateful to Dr. H. Markovitz for helpful comments on the manuscript and to Dr. G. C. Berry for supplying us with some of the data (in reference (8)) used for this analysis. Partial support for this project by the National Science Foundation is gratefully acknowledged.

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Received July 13, 1973
Revised July 20, 1973

EMPIRICAL EXTENSION OF THE MOLECULAR THEORY OF ROUSE TO THE VISCOELASTICITY OF BULK POLYMERS

Introduction

Various theories have been proposed to account for the viscoelastic plateau of bulk polymers or concentrated polymer solutions (1-5). As a rule, molecular chain entanglements, analogous to transient crosslinks or enhanced friction zones, are supposed to occur at widely separated points along the chains. Consequently, it is customary to derive an average entanglements distance from the dynamic properties, or from the break observed on logarithmic plots of viscosity against molecular weight (6).

However, if entanglements due to the formation of kinks, loops, or knots between the chains are really responsible for the pseudo-elastic behavior of hydrophobic polymers, there are strong objections to strict localization. Obviously, such couplings, being topological rather than due to chemical intermolecular forces, must correspond to very low energy barriers, easily overcome by the Brownian motion in the rubber-like state, so that this kind of molecular interaction must be of an essentially diffuse character.

To rely in this case, as is usually done, on an artificial concentration of the frictional resistance is far less justified than for the similar simplification of the bead spring theories valid for diluted polymers. In fact, a much larger divergence with an effectively smoother distribution of the dissipative intermolecular forces should then be expected, since the minimum number of segments approximately compatible with a Gaussian configuration of the submolecules is in general an order of magnitude lower than the corresponding number deduced from the entanglement "distances" M_e reported in the literature (6). Hence, the concept of entanglement "loci" is retained only as a possible limiting case in the analysis of dynamic properties briefly described below in terms of a straightforward extension of the Rouse model (7).

As a substitute for a lacking rigorous mathematical theory of the interactions of intertwined chains, instead of the value of the friction coefficient, it is the speed of the chain elements which is now changed by a general memory effect owing to the entanglements. Incidently, this semi-empirical approach coincides partly with Slomninskii's previous proposal (8) to introduce memory functions in a mechanical monoaxial model, instead of the tridimensional molecular one considered here.

Mathematical Structure of the Model and General Form of Its Dynamic Modulus

For brevity, only essential modifications of Rouse's original contribution will be indicated, using the notations of reference (7). Again, each molecular

chain of a mono-disperse polymer is supposed equivalent to an arbitrary number N of relatively short Gaussian submolecules, the junction points of which behave as isolated "frictional beads". According to Rouse, these beads are dragged by the surrounding medium with a speed equal to that of an affine continuum at the same point. It is now assumed that, in the presence of chain entanglements, there is another drag component which reflects the instantaneous cooperative effects, at time t after the beginning of any deformation, of even distant kinetic units disturbed at time $0 < \tau < t$ by one particular bead. Because they are damped by less and less direct chain couplings, through drifting intermingled structures, these long range interactions are globally represented for small perturbations by a Boltzmann-Volterra integral, the kernel of which will be, for the moment, left in the undetermined form of a "micro-memory" function F(t).

Let us apply to the system a sinusoidal shear $\alpha = \alpha_0 e^{j\omega t}$, of amplitude α_0 and pulsatance ω, in the x direction of the orthogonal axes x, y, z. The above hypothesis leads to the following set of partial differential equations which now gives the velocity components $\dot{x}(t)$, $\dot{y}(t)$, $\dot{z}(t)$ of the motion of the polymer molecules in various directions:

$$\dot{x}(t) = \dot{\alpha}(t)\, z\, \left[1 + \frac{h}{t_0} \int_0^t \frac{\dot{\alpha}(\tau)}{\dot{\alpha}(t)}\, F\, \frac{(t-\tau)}{t_0}\, d\tau\right] - B\bar{A}\, \{\nabla_x \mu\}$$

$$\dot{y}(t) = -\, B\bar{A}\, \{\nabla_y \mu\} \qquad (1)$$

$$\dot{z}(t) = -\, B\bar{A}\, \{\nabla_z \mu\}$$

As in the equations 10 of reference (7), μ is the thermodynamic potential of the molecules in a volume element of the 3 N configuration space, B the average coefficient of mobility of the beads, and $\bar{A}$ the square matrix which accounts for the coordination of the motions of successive submolecules. In addition, the delayed effects of the entanglement are now characterized by a time constant t_0 and a nondimensional parameter h of chain coupling efficiency. In steady state conditions, it may be shown, as in reference (7), that the solution of eq. (1) finally yields the complex modulus G*, or its normalized dimensionless form

$$G_R^* = G^* \frac{M}{\rho RT}$$

where M and ρ are the polymer molecular weight and density, T the absolute temperature, and R the gas constant:

$$G_R^* = Q^* (\omega_R, \tau_1, t_0, h) \sum_{p=1}^{N} \frac{j\omega_R(\tau_p/\tau_1)}{1 + j\omega_R(tp/\tau_1)} \qquad (2)$$

$p = 1, 2, 3, \ldots. N$

$\omega_R = \omega\tau_1$

The summation in this equation is simply the reduced modulus of Rouse's original theory, where τ_p represents the usual relaxation time corresponding to the mode P of the chain formed by the same number N of submolecules, τ_1 being the longest relaxation time. The new term Q^* is simply related to the memory function by the Laplace transform $L(j\omega)$ of $F(t)$:

$$Q^* = 1 + hL(j\omega) \tag{3}$$

For long chain polymers, the convergence of the series required to obtain non equivocal solutions independant of N should be expected. Notwithstanding the stricter conditions imposed in this respect by the shorter strands of polymer networks, the theory may still apply to cross-linked polymers. This transposition amounts to a combination of the strands-decoupling procedure of Chompff and Duiser (9), which takes into account the chain connectivity, and a modification of the boundary conditions of the matrix $\bar{A}$.

Furthermore, integration of eq. (2) in the complex plane shows that $h\tau_1/t_0\ F(t)$ is the limit at long times of the reduced stress relaxation function of the model.

Approximate Memory Function for Polystyrene

To derive quantitative predictions about the viscoelastic properties of polymers, it is necessary to somehow make explicit appropriate memory functions. In the case of narrow distribution polystyrenes, the stress relaxation data of Aklonis and Tobolsky (10) do not deviate considerably from the empirical expression:

$$F(t) = \left(\frac{t}{t_0}\right)^{-1/m} \cdot e^{-t/t_0} \quad m = C^{te} \tag{4}$$

the Laplace transform of which is a simple operator already classical in dielectric theory (11):

$$L(j\omega) = \Gamma\left(1 - \frac{1}{m}\right)/(j\omega t_0 + 1)^{1-1/m} \tag{5}$$

By substitution of eq. (5) into eq. (2), it is possible to calculate the reduced components G_R^1 and G_R^2 of the model complex modulus as a function of the reduced frequency ω_R, if the values of the three relevant parameters m, h, and t_0/τ_1 are specified. The values $h = 5 \times 10^3$ and $t_0/\tau_1 = 2.10^4$ have been chosen to fit at short and long times the experimental curves found by Onogi,

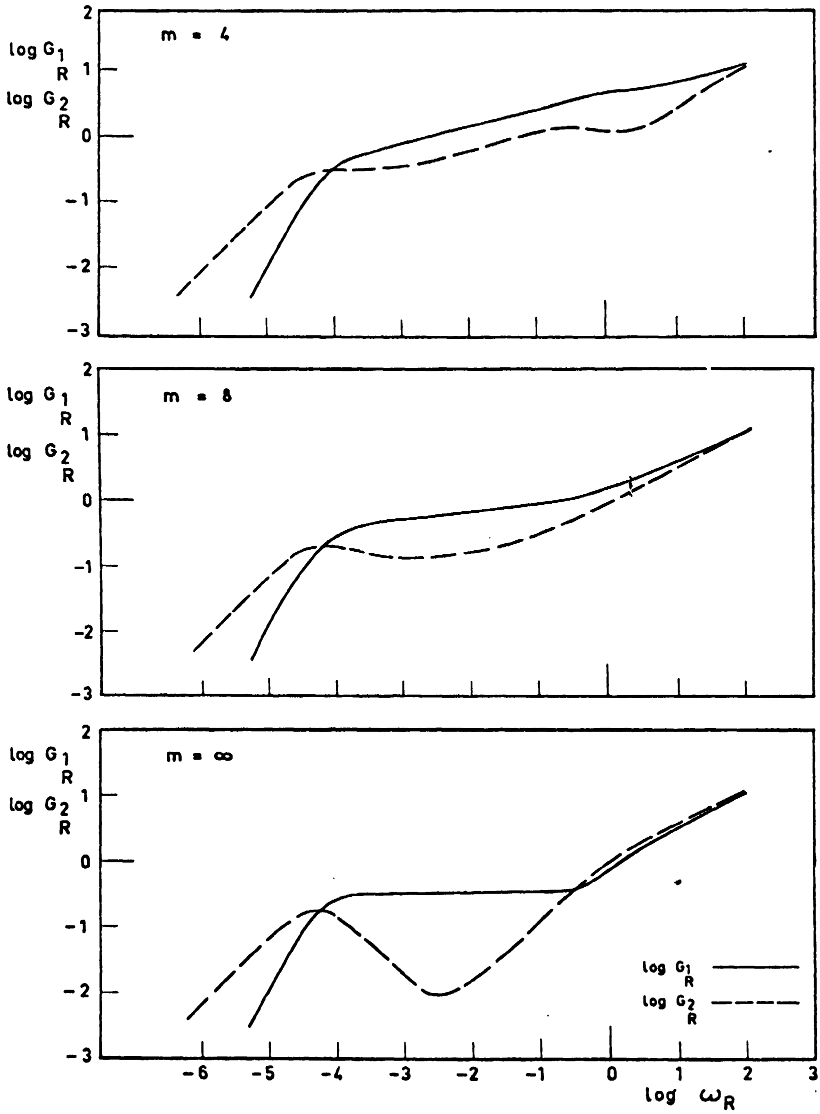

Fig. 1. Theoretical frequency dependence of the reduced dynamic moduli G_R^1 and G_R^2 of the model for $h = 5.10^3$ and $t_0/\tau_1 = 2.10^4$.

Masuda and Katagawa (12) for a typical narrow distribution polystyrene sample (L5) of molecular weight close to 270,000. The curves of the figure are examples of the theoretical dynamic properties in the "plateau" region for widely different values of m according to the present model. The comparison with the results of reference (12) shows that agreement is good in a large part of the "plateau", both for G_R^1 and G_R^2, for m = 8. This demonstrates that,

even with an approximate micro-memory function, it is possible to describe in this way the whole linear dynamic behavior of a bulk polystyrene of high molecular weight.

Formal Correspondence with the Notion of Entanglement Distance

In an attempt to clarify the possible structural signification of the parameters h and t_0, the dynamic viscosity G''/ω deduced from eqs. (2) and (4) at vanishing frequency has been compared with Graessley's (13) theoretical expression for the viscosity η of bulk polymers. Supposing that a simple chain slippage mechanism becomes acceptable in steady state conditions, their identification would be legitimate and give, after elimination of η:

$$1 + h\,\Gamma\,(1 - 1/m) = 0.262\,(M/M_e)^{2.5} \tag{6}$$

In the same manner, two expressions of the steady state compliance J_eo may be obtained either from eqs. (2) and (4), or from the application of the statistical elasticity theory to a pseudo-network with a molecular weight $M_e/2$ between cross-links; one gets by eliminating J_eo:

$$\frac{(1 - 1/m)}{\Gamma(1 - 1/m)} \cdot \frac{t_0}{h\,\tau_1} = \frac{\pi^2}{3} \cdot \frac{Me}{M} \tag{7}$$

Equations (6) and (7) point to a possible interdependence between h, t_0 and τ_1, and may provide a link between the current interpretation of chain entanglement effects by enhanced frictional points and the present approach.

The help of Y. Chevalier and T. Vinh, who performed the computation at the "Institut Supérieur des Matériaux et de Construction Mécanique", and fruitful discussions with Prof. J. D. Ferry and R. Chasset are gratefully acknowledged.

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Received July 10, 1973
Revised September 10, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 679–682 (1973)

SULFUR-CONTAINING POLYMERS. XI. REACTION OF BIS(DITHIOCARBONYL CHLORIDES) WITH DITHIOLS. A NEW ROUTE TO ALTERNATING COPOLYDISULFIDES

In a recent publication (1), we described the synthesis of alternating copolydisulfides by the reaction of bis(sulfenyl thiocarbonates) with dithiols in the presence of triethylamine. The process we call fragmentation polymerization involves thiol-induced fragmentation of sulfenyl thiocarbonate moieties in each step of the chain extension. We now wish to report a new type of the fragmentation polymerization which provides a convenient new synthetic route to alternating copolydisulfides.

The present process is outlined below:

$$\underset{\text{Ia, R = }-(CH_2)_4-\text{; b, R = }-(CH_2)_6-}{ClC(=O)SSRSSC(=O)Cl} + HSR'SH \xrightarrow[-COS,\ -HCl]{Et_3N} \underset{\text{II}}{\leftarrow RSSR'SS \rightarrow} \qquad (1)$$

The bis(dithiocarbonyl chloride) reactants (I) are easily prepared by the reaction of chlorocarbonylsulfenyl chloride with dithiols (2). Thus the net result is that chlorocarbonylsulfenyl chloride functions as a reagent for the co-oxidation of two dithiols.

Polymer formation was performed by adding dropwise a chloroform solution of I to a stirred solution of a dithiol (1 mole equivalent) and triethylamine (2 mole equivalents*) in chloroform below 10°C, followed by stirring the reaction mixture for 1 hr at room temperature. In the absence of triethylamine the reaction proceeded very slowly, showing that triethylamine acts not only as an acid acceptor but also as a catalyst. The results of polymerization are summarized in Table I. The copolymers thus obtained in good yields had inherent viscosities up to 0.75. In the infrared spectra of copolymers, the absorption bands due to sulfenyl dithiocarbonate linkage were completely absent, excluding the presence of significant amounts of recurring unit (III), which may be formed by ordinary polycondensation reaction of I with dithiols. Fur-

$$\leftarrow RSSC(=O)SR'SC(=O)SS \rightarrow$$

III

*In practice, it is convenient to carry out the polymerization in the presence of a small (1 to 5%) excess of triethylamine.

TABLE I

Alternating Copolydisulfides

Polymer No.	I R	Dithiol R'	Yield, %	Mp, °C[a]	η_{inh}[b]
IIa	$-(CH_2)_4-$	$-(CH_2)_2-$	91	88	0.66
IIb	$-(CH_2)_4-$	$-(CH_2)_3-$	80	53	0.53
IIc	$-(CH_2)_4-$	$-(CH_2)_8-$	89	45	0.44
IId	$-(CH_2)_4-$	$-(CH_2)_9-$	96	48	0.48
IIe	$-(CH_2)_4-$	$-(CH_2)_{10}-$	90	58	0.28
IIf	$-(CH_2)_6-$	$-(CH_2)_2-$	96	107	0.63
IIg	$-(CH_2)_6-$	$-(CH_2)_3-$	85	—	0.73
IIh	$-(CH_2)_6-$	$-(CH_2)_4-$	94	38	0.75
IIi	$-(CH_2)_6-$	$-(CH_2)_8-$	94	43	0.61
IIj	$-(CH_2)_6-$	$-(CH_2)_9-$	91	48	0.41
IIk	$-(CH_2)_6-$	$-(CH_2)_{10}-$	98	46	0.39

[a]Determined by DTA.
[b]In sym-tetrachloroethane (0.5%, 30°C).

thermore, elemental analyses and the NMR spectra of the polymers were consistent with the 1:1 copolydisulfide structure.

The following two pathways (A and B) are conceivable for the formation of copolydisulfides from I and dithiols.

A. Direct formation of a disulfide bond by thiol-induced fragmentation of a dithiocarbonyl chloride linkage:

$$\sim R{-}S{-}S{-}\underset{\underset{O}{\|}}{C}{-}Cl \quad + \quad H{-}S{-}R'\sim \quad \xrightarrow[-HCl]{-COS} \quad II \qquad (2)$$

B. Initial formation of a sulfenyl dithiocarbonate bond followed by its reaction with HS~ group leading to a disulfide bond:

$$HSR'SH \xrightarrow{-HCl} \sim S{-}S{-}\underset{\underset{O}{\|}}{C}{-}S{-}R'{-}S{-}\underset{\underset{O}{\|}}{C}{-}S{-}S{-}R\sim \xrightarrow[-COS]{HSR'} \qquad (3)$$

III

$$\sim RSSR'\sim \quad + \quad \sim S{-}S{-}\underset{\underset{O}{\|}}{C}{-}S{-}R'SH \longrightarrow II$$

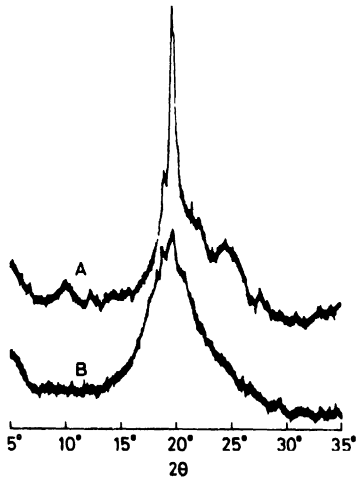

Fig. 1. X-ray diffraction patterns of (A) polymer IIj; (B) random copoly-(hexamethylene-nonamethylene disulfide).

An effort was made to obtain some information on the reaction pathway. When the reaction of Ib with ethanedithiol was conducted at -60°C, a polymer containing both recurring units II and III ($R = -(CH_2)_6-$, $R' = -(CH_2)_2-$) was obtained. Its infrared spectrum showed bands at 1710, 1640, 880, and 830 cm^{-1} characteristic of sulfenyl dithiocarbonate group in addition to the bands characteristic of the copolydisulfide. Analysis for carbon indicated a 2:1 ratio of II:III. On treatment with triethylamine the polymer gave the corresponding copolydisulfide with quantitative loss of carbonyl sulfide. These findings would suggest that the present polymerization proceeds, at least in part, according to eq. (3).

Whatever the polymerization pathway, this process gives essentially alternating copolydisulfides as can be seen from eqs. (2) and (3), provided the redistribution of disulfide bonds is not operative. For comparison purposes, a random copolydisulfide of 1,6-hexanedithiol and 1,9-nonanedithiol was prepared by the oxidative coupling of an equimolar mixture of the dithiols with bis-(methoxycarbonyl) disulfide (3). The inherent viscosity of the polymer in sym-tetrachloroethane was 0.34. Both the random copolymer and IIj containing the same composition were characterized by DTA and x-ray. DTA was used to determine the melting points of the polymers. The melting point of copolymer IIj (48°C) is higher than that of the random copolymer (36°C), indicating its regular structure. As shown in Fig. 1, IIj is highly crystalline and the random copolymer is almost amorphous. The noticeable difference in the crystallinity of the two copolymers strongly supports the presence of an essentially alternating arrangement of 1,6-hexanedithiol and 1,9-nonanedithiol moieties. This means that redistribution of disulfide bonds had not occurred to a significant extent under the specified polymerization conditions.

Thus the present process provides a convenient new route to alternating copolydisulfides. The key synthetic merits are that bis(dithiocarbonyl chloride) intermediates are easily prepared from chlorocarbonylsulfenyl chloride and dithiols, and high molecular-weight polymers can be obtained in good yields.

Experimental

Bis(dithiocarbonyl chlorides) (I) were prepared by the reaction of chlorocarbonylsulfenyl chloride with dithiols as described previously (2). The reaction of I with dithiols was carried out in chloroform. Table I gives a survey of the results. As a typical example, the reaction of Ia with 1,9-nonanedithiol is described in detail.

To a stirred solution of 3.09 g (16.1 mmole) of 1,9-nonanedithiol and 3.30 g (32.7 mmole) of triethylamine in 30 ml of chloroform was added dropwise a solution of 5.00 g (16.1 mmole) of Ia in 15 ml of chloroform below 10°C. At the completion of the addition, the reaction mixture was warmed slowly to room temperature, and stirring was continued for 1 hr. The mixture was concentrated, and washed 5 times by kneading with 100-ml portions of methanol. The product was dried and then reprecipitated from chloroform into methanol. The yield was 4.79 g (96%), mp 48°C; η_{inh} 0.48 (in sym-tetrachloroethane); the infrared spectrum showed no signals in the carbonyl region; NMR ($CDCl_3$) δ 1.1-2.0 (m, 18H), 2.68 (t, 8H).

Analysis calculated for $(C_{13}H_{26}S_4)_n$: C, 50.27%; H, 8.44%; S, 41.29%. Found: C, 50.13%; H, 8.37%; S, 41.19%.

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Received July 19, 1973
Revised August 21, 1973

THE PHOTODEGRADATION OF POLY(1,3-PHENYLENE ISOPHTHALAMIDE) FILMS IN AIR

Poly(1,3-phenylene isophthalamide), PPiPA, is produced by DuPont under the trade name of Nomex, and is now widely used in the form of fiber or paper for applications where high modulus, high temperature resistance, and/or inherent nonflammability are essential (1). However, the uses of PPiPA in outdoor applications (protective clothing, webbing, etc.) or in the presence of any near ultraviolet radiation (aircraft interior furnishings, etc.) are limited by the rapid deterioration which results on exposure of this polymer to terrestrial sunlight. This ultraviolet (UV) sensitivity is illustrated in Figure 1, which shows that unstabilized Nomex yarns lose 60% of their initial elongation to break in 100 hr of xenon arc irradiation (roughly comparable to noon summer sunlight). In this paper, we report some preliminary data from an investigation into the nature and origin of some of the chemical changes leading to this deterioration.

PPiPA films were cast from N,N-dimethylacetamide-calcium chloride solutions, washed and dried to give 10 μ films (<0.04 wt % Ca^{++}), as described previously (2). Films prepared from solutions of the commercial Nomex fibers and those prepared from laboratory polymerizations of 1,3-phenylene diamine and isophthaloyl chloride showed identical UV, IR, and NMR spectra, and identical photodegradation changes. Similarly, the use of dimethylsulfoxide as the casting solvent or inclusion of Ca^{++} concentrations up to ~1 wt % caused no change in the degradative behavior. The 10 μ films were irradiated in a 2500 watt Atlas xenon arc Weather-Ometer at 30% relative humidity.

Transmission infrared (IR) spectra of the air irradiated films showed only a small shoulder at ~1720 cm^{-1} as a result of Xe arc irradiation. However, at-

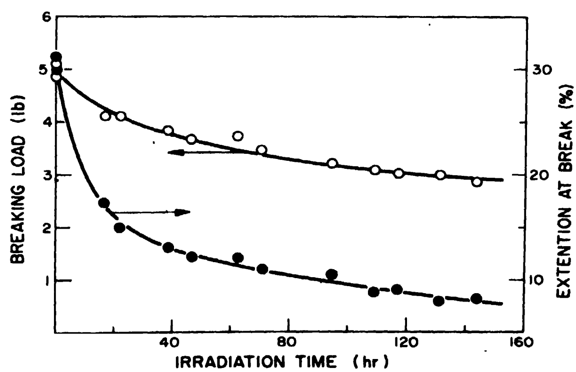


Fig. 1. Effect of UV irradiation on the tensile properties of Nomex yarns. Irradiation in an Atlas 2500 watt Xe arc Weather-Ometer. Two ply 22 tex yarns irradiated in air at 30% relative humidity.

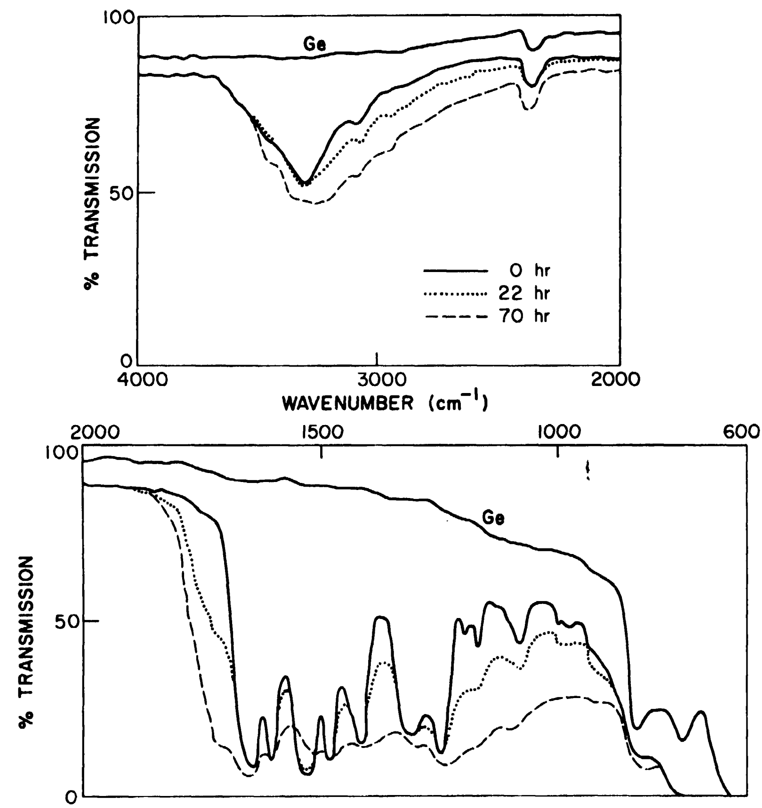


Fig. 2. ATR IR spectra of air irradiated PPiPA films. Ge reflection element, 45° incidence. Film surface facing Xe arc.

tenuated total reflection (ATR) IR on a germanium reflection element at 45° angle of incidence (beam depth of penetration 0.4 μ into the film surface (3)) showed marked changes in the surface IR of the film side towards the xenon arc (Figure 2); the obverse side of the film showed little change up to complete mechanical failure of the films (~120 hr irradiation). The ATR IR techniques have been described previously (3). The most prominent changes in the ATR spectra are the large absorption increase at ~1720 cm^{-1} (shown later to be due to carboxylic acid groups), the drop in the 1530 cm^{-1} amide –NH– absorption (4) and the increased absorption at ~3250 cm^{-1}.

The surface IR changes accompanying photodegradation are most clearly shown in the differential spectrum A (Fig. 3) which was obtained with an unirradiated film in the reference beam and a 114-hr irradiated film in the sample beam of the spectrometer, both films mounted identically on germanium reflection elements. The new absorption at 1720 cm^{-1} is clearly visible, together with one at 1370 cm^{-1}. The shoulder at 1650 cm^{-1} probably results from imperfect cancellation of the intense amide $\gtrless$C=O absorption.

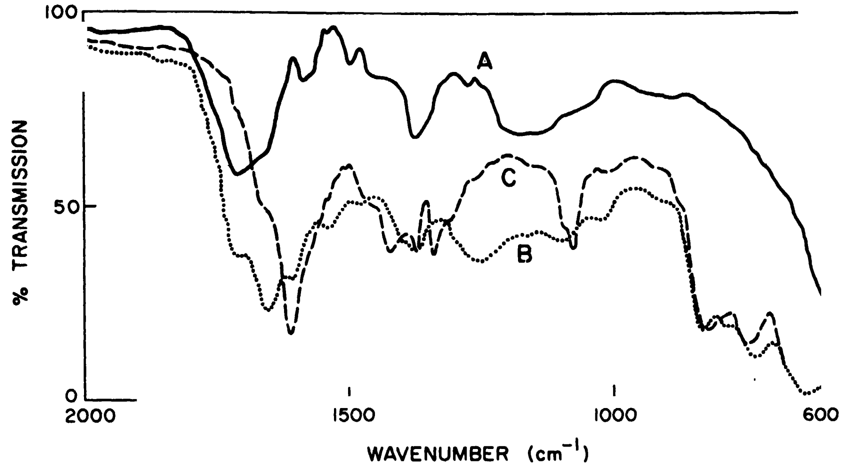


Fig. 3. ATR IR spectra of photo-oxidized PPiPA films. Ge reflection element, 45° incidence, 114 hr Xe arc irradiation. A. Differential spectrum, UV irradiated PPiPA vs. unirradiated film. B. Ethanol extract of irradiated film, evaporated onto reflection element. C. Ethanol extract of irradiated film, after concentrated aqueous NaOH treatment, evaporated onto reflection element.

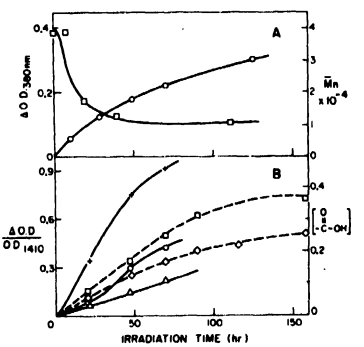


Fig. 4. Changes on UV irradiation in air of PPiPA films. A. –o–, O.D. increase at 380 nm; –□–, $\bar{M}n$ decrease. B. ATR IR changes: –x–, 1720 cm^{-1} increase; –o–, 1530 cm^{-1} decrease. Transmission IR change: –Δ– 1720 cm^{-1} increase. Overall [–COOH] increase: –□–, from potentiometric titration; –◇–, from transmission IR data.

The IR changes accompanying photodegradation are plotted against time in Figure 4. Normalized optical densities ($\Delta OD/OD_{1410}$) are used so as to compensate for variations in the film-germanium element contact and to allow direct comparison with the transmission IR data (3) (the 1410 cm^{-1} absorption was found to be invarient throughout the degradation).

The unirradiated 10μ PPiPA films absorb completely all UV below 355 nm (2). On irradiation, this UV cut-off moves towards the visible, and the absorption tail extends progressively out into the visible, but remains featureless. The increased absorption of this tail is shown at 380 nm (arbitrarily chosen) in Figure 4. This is largely responsible for the yellow-brown coloration of the air irradiated PPiPA films and fibers.

Number average molecular weights ($\bar{M}n$) of irradiated films were determined in N,N-dimethylacetamide solution on a Hewlett-Packard High Speed Osmometer with a cellulose ester membrane (Schleicher and Schvell, 0.005μ pore size). These $\bar{M}n$ values are shown in Figure 4, although the lowest values are somewhat uncertain owing to back diffusion.

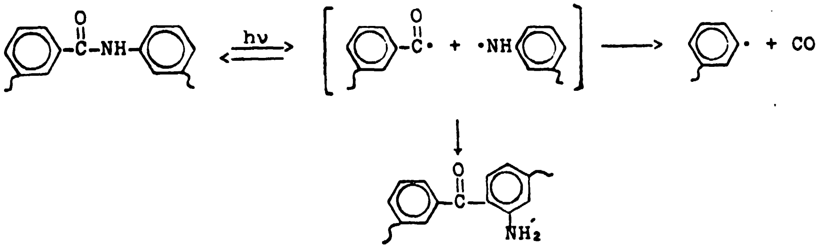
The observed ATR IR changes indicate rapid photodegradation of a thin ($\sim 0.5\mu$) layer of the irradiated PPiPA film surface. Consequently the drop in $\bar{M}n$ probably results entirely from chain scission in this surface layer with the remainder of the film largely undegraded. The $\bar{M}n$ of ~10,000 after ~50 hr of irradiation would then require a local $\bar{M}n$ of ~1200 in the degraded surface layer ($\sim 0.5\mu$), i.e., oligomeric material containing only 5-6 amide links.

Extensive surface chain scission was confirmed by prolonged ethanol extraction of a 114-hr irradiated film (~150 cm^2). Although undegraded PPiPA is completely insoluble in ethanol, when the extract was concentrated by evaporation on the faces of a germanium ATR element, it then showed the spectrum B in Figure 3. This extract spectrum is very similar to the differential film spectrum A. Treatment of the ethanol extract with concentrated aqueous NaOH, resulted in spectrum C. The loss of the 1720 cm^{-1} absorption (in B) and generation of the 1610 cm^{-1} absorption (in C) indicates that the 1720 cm^{-1} absorption is due to aromatic carboxylic acid groups which give $-COO^-$ in the presence of a base (4). Similarly the 3250 cm^{-1} absorption (Fig. 2) probably results from the carboxylic –OH group (4). Neither of these absorptions was detected after PPiPA irradiation in the absence of O_2 (2).

Good agreement was found between –COOH concentrations estimated from the transmission IR absorption at 1720 cm^{-1} (using an experimental extinction coefficient for monomeric benzoic acid in dioxane of 610 M^{-1} cm^{-1}) and values derived from potentiometric titrations of irradiated films (100 cm^2) in carefully purified N,N-dimethylacetamide (Fig. 4). The quantum yield for carboxylic acid group formation was found to be 1-2 $\times$ 10^{-4} m. $einst.^{-1}$ from both the bulk IR changes and the surface IR changes. Calculated surface $\bar{M}n$ values based on one –COOH end per chain agree quite well with the values calculated from the osmometry data. The levelling off of both the UV absorption increase and the surface IR changes with irradiation time probably results from the filtering effect of the yellowed, degraded surface layer of each film. Also the decrease in the surface amide concentration (Fig. 4) as measured by the 1530 cm^{-1} absorption (IR extinction coefficient found experimentally to be 110 M^{-1} cm^{-1}) indicates close to quantitative conversion to –COOH end groups.

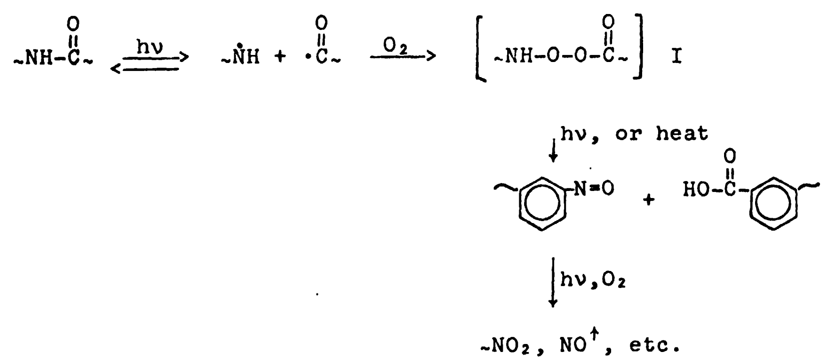
We have previously reported on the UV degradation of PPiPA films in the

absence of oxygen (2) and shown that the primary photolysis process is probably a scission of the amide link to give two radicals [reaction (1)]. In the absence of O_2 each radical pair can either recombine directly, eliminate carbon monoxide (quantum yield ~1 X 10^{-6} m. einst.$^{-1}$) or recombine to give a 2-aminobenzophenone backbone unit (a photo-Fries rearrangement), reaction (1). Appreciable crosslinking also occurs under vacuum irradiation but tensile properties of fibers are unaffected (cf. Fig. 1).



(1)

No photo-Fries product was detected after irradiation in air, since the characteristic UV absorption at 410 nm and fluorescence emission at 460 nm (2) were absent. Similarly gel was not formed in air irradiated PPiPA films as shown by the rapid, complete dissolution of the degraded films in N,N-dimethylacetamide. The air irradiation results can most readily be rationalized in terms of an initial amide scission (as in reaction 1) followed by O_2 coupling with the radical fragments (reaction 2).



(2)

The transient peroxide intermediate (I) might well be formed, since the radical pair will be trapped together in the rigid polymer matrix (T_g ~280°C (5), but (I) will eventually cleave by photolysis or thermal decomposition to give the observed carboxylic acid, and possibly a nitroso derivative. However, nitroso groups are extremely unstable both to UV cleavage, UV and thermal oxidation (to $-NO_2$ etc.) and coupling reactions (6), so it is unlikely that a significant stationary concentration exists during photolysis. The 1370 cm^{-1} absorption in the differential and extract spectra (A and B, Fig. 3) is consistent

with an N–O group (nitro or nitroso) (4), and some NO gas was detected by gas chromatography from the vacuum irradiation of an air irradiated film.

The surface nature of the photodegradation results from the large inherent UV absorption of the PPiPA (~40% of the incident Xe arc energy is absorbed in the first $0.4\,\mu$ of a $10\,\mu$ film) and similar surface effects have been observed in polyethylene terephthalate (7). However, degradation to give yellowing and –COOH groups ($\phi \sim 1 \times 10^{-4}$ m. einst.$^{-1}$) was observed, although at a very low rate even when wavelengths $\geq$ 360 nm were used, and degradation was roughly uniformly distributed throughout the film under these conditions. The failure to detect even a low concentration of 2-aminobenzophenone groups after air irradiation may indicate either that the O_2 scavenging of radicals after amide scission largely prevents recoupling at the 2-position, or that these groups are destroyed in a subsequent photolysis. In fact, 2-aminobenzophenone photolyzes rapidly in strongly hydrogen bonding solvents (8).

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Revised August 21, 1973

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Issued as NRCC No. 13563.

POLYMER LETTERS EDITION VOL. 11, PP. 689–694 (1973)

A NEW TYPE OF ELASTOMER DERIVED FROM CHRYSOTILE ASBESTOS

We have shown in a recent publication (1) that new composite polymeric materials of outstanding mechanical properties have been synthetized by grafting a polymeric chain on the stripped polymeric siloxanic plane of phyllosilicates, such as chrysotile asbestos. The coupling agent was a vinyl-siloxy radical, derived from methyl-vinyl-dichlorosilane, and grafted by a condensation reaction on the siloxanic plane of the phyllosilicate after elimination of the octahedral layer by acid leaching (2).

Instead of using methyl-vinyl-dichlorosilane as a coupling agent, in this work we used monofunctional dimethyl-allyl-chlorosilane. After an acidic treatment of the chrysotile asbestos for 56 hours at 50°C, we obtained a rubbery material, while in the same experimental conditions but with methyl-vinyl-dichlorosilane, a non rubbery fiber-like mineral derivative was synthetized.

Intrigued by this particular behavior of the allylic derivative of Cassiar A.K. chrysotile, we tried to vulcanize it with benzoyl peroxide in the same way as we did for the grafted copolymers (1). This experiment led us to a material which exhibits all the characteristics of an elastomer.

In this paper of limited scope, we are reporting some of the experiments which weie carried out to explain the rubbery behavior of the allylic derivative of chrysotile-asbestos. Till now, our experiments were rather limited by the very high price of allyl-dimethyl-chlorosilane.

Experimental

The chrysotile-asbestos used in this work was Cassiar A.K. chrysotile asbestos. Its structure and surface properties have been described by Fripiat and della Faille (3). Its calculated structural formula is the following:

$$Mg_6Si_4O_{9.46}(OH)_{9.17}$$

The synthesis of the allylic derivative of Cassiar A.K. chrysotile asbestos was carried out in accordance with a procedure described in a previous publication (2). The reaction takes place at 50°C over a period of 56 hours.

The components of the reaction mixture were these:

Dried chrysotile asbestos	3 g
Hydrochloric acid (37%, reagent grade)	120 ml
Isopropanol (reagent grade)	120 ml
Allyl-dimethyl-chlorosilane	5 ml

The allylic derivative of Cassiar A.K. used in this study has the following composition:

$$[Si_4O_{10}Mg_6(OH)_8]_{0.10}[Si_4O_{10}(\underset{Me}{\overset{Me}{Si}}-CH_2-CH{=}CH_2)_4]_{0.29}\ [Si_4O_{10}H_4]_{0.61}$$

The formula has been divided into three components: the first one corresponds practically to the non hydrolyzed portion of the mineral; the second one to the hydrolyzed grafted part, and the third one to the hydrolyzed non-grafted fraction. About one third of the silanol group generated by the hydrolysis were replaced by allyl-dimethyl-siloxy radicals. The crude allylic derivative contained 33% (by weight) of tetramethyl-diallyl-disiloxane which results from the condensation of a part of the dimethyl-allyl-chlorosilane. This fraction may be extracted with benzene in a Soxhlet apparatus.

The crude allylic derivative (unextracted) was milled at room temperature in a Rapra Micromill with 2% of benzoyl peroxide and vulcanized at 145°C for 10 min under a pressure of 800 kg. cm^{-2}.

A Du Pont Differential Scanning Calorimeter coupled with a Du Pont Thermal Analyzer was utilized to study the thermal behavior of the allylic derivative.

The isochronal variation of the modulus of elasticity was obtained by the Gehman procedure standardized according to the A.S.T.M. Standard (4). The measurements were taken after 10 sec had elapsed and the results reported in the form of 3 G(10).

Results

The allylic derivative of Cassiar AK chrysotile asbestos is a mixture of grafted phyllosilicate and of diallyl-tetra-methyl-disiloxane.

The mechanism of the condensation reaction which was studied in detail in a previous publication (1) may be schematized by the following equations:

$$\equiv Si-O-Mg-OH + 2H^+ \rightarrow \equiv Si-O-H + Mg^{++} + H_2O \qquad (1)$$

$$\equiv Si-O-H + CH_2{=}CH-CH_2-\underset{Me}{\overset{Me}{Si}}-Cl \xrightarrow{H^+} \equiv Si-O-\underset{Me}{\overset{Me}{Si}}-CH_2-CH{=}CH_2 + HCl \qquad (2)$$

$$2CH_2{=}CH-CH_2-\underset{Me}{\overset{Me}{Si}}-Cl + H_2O \rightarrow (CH_2{=}CH-CH_2-\underset{Me}{\overset{Me}{Si}})_2-O + 2HCl \qquad (3)$$

In eq. (1), the octahedral brucite layer of the mineral is eliminated and silanol groups are generated on the surface of the tetrahedric siloxanic plane. In eq. (2), the generated silanol reacts with a molecule of dimethyl-allyl-chlorosilane and dimethyl-allyl-siloxy groups are grafted. The third step is a parasite reaction which produces tetramethyl-diallyl-disiloxane.

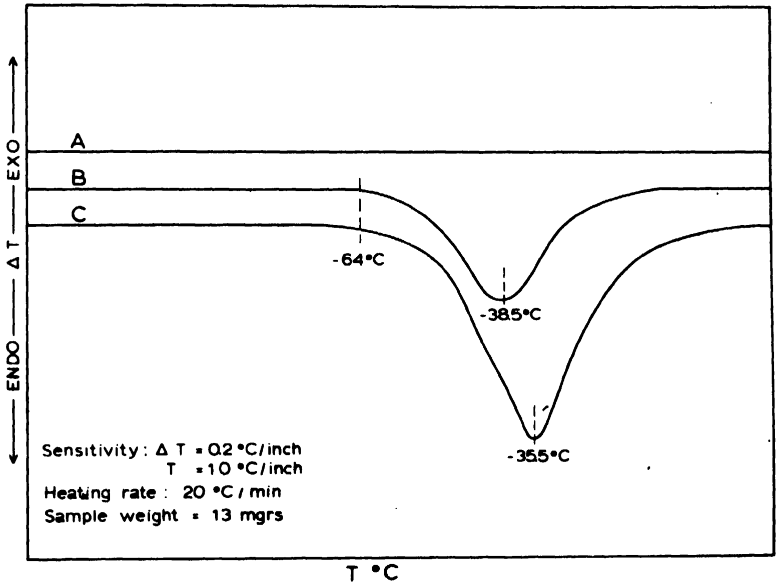

Fig. 1. Differential scanning calorimetry of the allylic derivative of chrysotile-asbestos: (a) extracted; (b) vulcanized; (c) unextracted.

The pure allylic derivative obtained after elimination of the disiloxane fraction by extraction is not rubbery and cannot be vulcanized. It appears thus that the rubbery character of this organo-mineral derivative is closely linked to the presence of soluble tetramethyl-diallyl-disiloxane, which may act as a plasticizer for the grafted siloxanic plane derived from the phyllosilicate.

With the object of clarifying this point, we have submitted to the Differential Scanning Calorimetry a sample of the crude allylic derivative, a sample of the extracted product, and a sample of the vulcanized material. The thermogram of the unextracted derivative (Fig. 1C) is characterized by a strong endotherm which corresponds to a fusion. This endotherm starts around −65°C and has its maximum located at −35°C. The absorbed heat which is associated with the melting phenomenon is equal to 3.2 calories per gram of the crude derivative. In some thermograms, we sometimes noticed an exothermic peak located at a lower temperature (−90°C) which corresponds with a crystallization. Since the thermogram of the extracted product (Fig. 1A) is completely linear, the endotherm of thermogram C should be the result of the melting of the tetramethyl-diallyl-disiloxane. The thermogram of the vulcan-

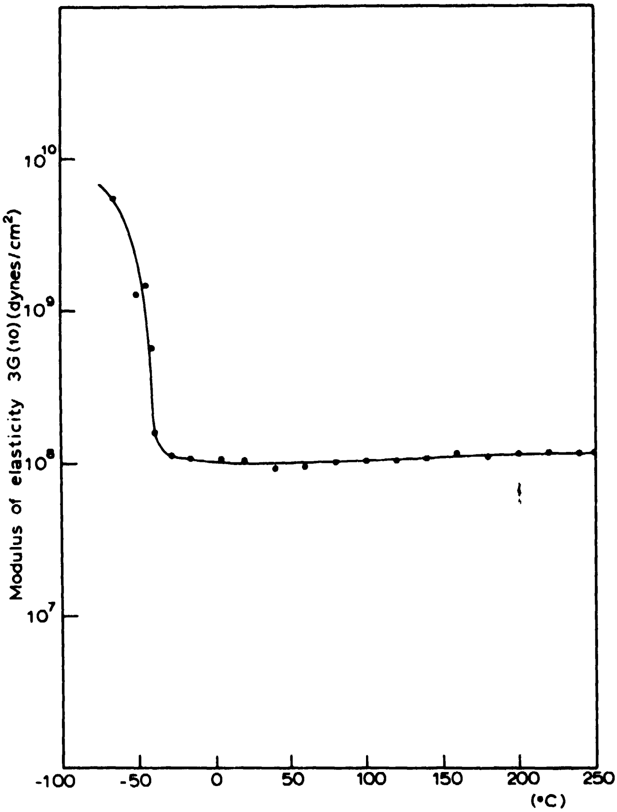

Fig. 2. Modulus (3G) – temperature curve (10 sec modulus) of the vulcanized allylic derivative of chrysotile-asbestos.

ized allylic derivative (Fig. 1B) is also characterized by an endotherm, but in this case the heat evolved (1.6 cal/gr^{-1}) is less important than in the case of the crude unvulcanized derivative. This result indicates that during the vulcanization around 50% of the tetramethyl-diallyl-disiloxane has disappeared or has undergone a reaction of copolymerization with the dimethyl-allyl-siloxy radicals grafted on tetrahedric siloxanic planes of the mineral framework.

The isochronal modulus-temperature curve of the vulcanized allylic derivatives was determined according to the Gehman procedure (4). The result of this study is reported in Figure 2. This curve shows that the allylic derivative of Cassiar A.K. displays all the characteristics of an elastomer. One notices principally the very long rubbery plateau which is completely linear from –25 to 250°C. Unfortunately, because of the limitation of our Gehman apparatus, experiments at temperatures higher than 250°C were impossible. The rapid increase of the modulus at temperatures lower than –40°C is to be attributed to the freezing of the tetramethyl-diallyl-disiloxane. This transition corresponds to the endotherm peak noticed by D.S.C. (Fig. 1B).

Discussion

The presence of a very long and steady rubbery plateau in the modulus-temperature curve of the vulcanized allylic derivative constitutes for us the best evidence of the existence of a tridimensional rubbery network in the material. Since the major fraction of the brucite layers of the phyllosilicate were eliminated by acid leaching, the allylic derivative is constituted mainly of a mixture of the polysiloxanic planes, on which dimethyl-diallyl-disiloxy radicals are grafted, and of tetramethyl-diallyl-disiloxane. It is likely that the flexible polysiloxanic planes play the same role in this type of rubber as the linear flexible polymer chain in traditional elastomers. The residual tetramethyl-diallyl-disiloxane would be a plasticizer for these elastic plane.

We have noticed that after vulcanization, the melting peak is reduced to about half of its initial value (Fig. 1B). This result may provisionally be interpreted in the following way: according to the literature (5), tetramethyl-diallyl-disiloxane has a boiling point higher than 200°C and loss of this product by evaporation during the course of the vulcanization process is practically impossible since the reaction is carried out at 145°C in a closed mold. It is therefore very likely that about 50% of the tetramethyl-diallyl-disiloxane present in the crude derivative has been copolymerized with the dimethyl-allyl-siloxy radicals grafted on the siloxanic plane; therefore these siloxanic planes are joined by short chains of polytetramethyl-diallyl-disiloxane.

It was also shown that the vulcanized allylic derivative maintains its rubbery properties at least up to a temperature of 250°C. The great stability of this tridimensional network may be attributed to the low carbon content (23%) and to the ladder structure of the bidimensional siloxanic framework, which constitutes the base of this elastomer.

Conclusion

The results reported in this note show that the organo-mineral polymeric material consisting of the two dimensional siloxanic framework of the phyllosilicate, having unsaturated polymerizable radicals linked by Si-O-Si siloxane bonds, may constitute the base of an elastomer.

Considering the rather limited scope of our experiments, we are of the opinion that the interpretation given here of the rubbery behavior of this kind of material should be taken on a provisional basis. Nevertheless, we believe that the results of this study open new fields of research to the polymer chemist.

Summary

This note describes briefly the synthesis and some thermomechanical properties of an elastomeric composite material derived from chrysotile-asbestos.

We wish to acknowledge the financial support of the I.R.S.I.A. and of the Society Eternit (Kapelle-op-den-Bos).

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Received May 25, 1973
Revised August 7, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 695–700 (1973)

CHARGE-TRANSFER COMPLEXES OF 3,5-DINITROBENZOYL COTTON CELLULOSE

Introduction

The interaction of a suitably "electron rich" molecule with an appropriate "electron deficient" partner results in the formation of a charge-transfer (donor-acceptor) complex. This phenomenon is well known in organic chemistry (1,2).

In recent years the preparation and properties of synthetic donor or acceptor homopolymers have received considerable attention (3,4,5). In contrast, a survey of the literature reveals that the synthesis of macromolecular donors or acceptors through modification of naturally occurring polymeric materials such as cellulose has received only scant attention. Though cellulose derivatives with the potential to form charge-transfer (CT) complexes have been prepared (6,7,8), only one attempt to study the subsequent complexation of such derivatives has been reported. Recently, Avny et al. (9) have shown that anisidine (a donor) was adsorbed by trinitrobenzyl and trinitrophenylethyl cellulose ethers (acceptors), but found no complexation of naphthalene, a well-documented π-donor. The observed adsorption was interpreted as evidence for n-type complexes.

CT complexes are typically characterized by a weak bond. However, their formation is often accompanied by salient changes in the physical and chemical properties of the two species of which they are composed. Therefore, we have recently undertaken the syntheses of cellulose derivatives that can form CT complexes.

In the present communication, we report some preliminary results on the preparation and novel properties of one such chemically modified cellulose, 3,5-dinitrobenzoyl cotton cellulose (DNBC). We have found that DNBC readily interacts with a variety of donors to form DNBC acceptor polymer-donor monomer CT complexes. To our knowledge this is the first reported example of a cellulose derivative that forms CT complexes with a broad range of donors.

Experimental

The cellulose was loose twist 12/3 (tex-151) Pima kier boiled cotton yarn.

DNBC was prepared by immersing a skein of untreated yarn weighing 2.60 g in a glass stoppered flask containing 7.35 g of 3,5-dinitrobenzoyl chloride in a mixture of 50 ml DMF and 5 ml pyridine. The reaction mixture was shaken mechanically at room temperature for the desired length of time. The reaction was quenched by immersing the yarn in 100 ml DMF for 15 min. The yarn was then washed with tap water for 30 min, oven dried at 80° for

TABLE I

Degree of Substitution Versus Reaction Time for the 3,5-Dinitrobenzoylation of Cotton Cellulose Yarn

Reaction Time (hrs)	% Wt. Gain	% N[a]	Th. % N[b]	D.S.[b]
1	1.5	0.40	0.53	0.02
3	10.3	1.49	1.26	0.08
5	20.7	2.50	2.30	0.16
6.5	32.3	3.49	3.39	0.26
16.0	65.0	5.66	5.38	0.51
24.0	90.0	6.51	6.38	0.69
40.0	117	7.40	7.37	0.92
40.0	128	7.89	7.69	1.01
54.0	133	7.96	7.85	1.06

[a]Kjeldahl
[b]Based on weight gain.

15 min, and allowed to equilibrate at ambient conditions for 24 hr before weighing. The D.S. values reported in this study (Table I) are based on weight gain.

Complexation of the various donors by DNBC samples of known weight (400-800 mg) and D.S. was accomplished by immersing the yarn in a 50-ml ethanolic solution of donor for 24 hr. All experiments were conducted at room temperature (25° ± 1°C). After equilibration, the complexed DNBC sample was removed from the solution and dipped for about 1 sec in ethanol to remove any residual donor solution adhering to the surface. The amount of donor complexed was determined by weight gain, after allowing the yarn to dry at ambient conditions for 24 hr. A slight correction in this determination was necessary because of a weight loss of 0.60 ± 0.30% when DNBC was treated with ethanol and allowed to dry. Control experiments, in which samples of untreated cotton yarn were immersed in donor solutions of the same concentration used to obtain the data reported in Tables II and III, showed negligible adsorption of donor (experimental limits ±0.5%).

Results and Discussion

Table I shows the D.S. achieved as a function of time when cotton yarn was esterified with 3,5-dinitrobenzoyl chloride in a DMF-pyridine mixture at room temperature under a specified set of conditions. By this method DNBC

TABLE II

The Adsorption of Various Donor Monomers by 3,5-Dinitrobenzoyl Cotton Cellulose Yarn[a]

Donor	% Wt. Gain	f	% N[b]	Th. % N[c]	Color
Naphthalene	2.5	0.10	-	7.14	pale yellow
1-Methylnaphthalene	3.1	0.11	7.30	7.09	yellow
2-Naphthol	2.8	0.10	7.27	7.09	yellow
Mesitylene	0.2	0.03	7.32	7.31	colorless
Biphenyl	2.6	0.09	6.92	7.11	colorless
Benzidine	4.4	0.11	7.76	7.78	dark brown
p-Anisidine	4.4	0.16	7.50	7.57	brown
N,N-Dimethylaniline	3.1	0.12	-	7.53	red-brown
Indole	2.9	0.12	7.58	7.54	orange-yellow
Acenaphthene	3.7	0.11	6.92	7.06	golden yellow
Control[d]	-0.9	0.00	7.40	7.37	colorless

[a]D.S. = 0.92.
[b]Kjeldahl.
[c]Based on weight gain.
[d]DNBC immersed in ethanol and dried at ambient conditions.

TABLE III

Percent Weight Increase Versus Indole Concentration[a]

Indole (M)	% Weight Increase	f[b]
0.00	-0.06	0.000
0.20	3.07	0.113
0.40	5.71	0.191
0.60	7.13	0.234
0.80	9.31	0.300
1.00	9.80	0.335
1.50	13.5	0.426

[a]DNBC had a D.S. of 1.01.
[b]Determined from weight gain.

can be conveniently prepared in D.S. of approximately 1.0 with very little discoloration of the yarn.

The results of complexation studies in which DNBC was treated with 0.20M ethanolic solutions of various donors are summarized in Table II. In this table the symbol f represents the fraction of the total moles of 3,5-dinitrobenzoyl acceptor sites on the cellulose that are occupied by the particular donor. The results presented in this table clearly show that DNBC complexes π-type donors such as naphthalene or indole. This finding was somewhat surprising since Avny et al. (9) had previously reported that trinitrobenzyl and trinitrophenylethyl cellulose did not form a π-type CT complex with naphthalene.

In addition to observing the adsorption of various monomeric donors from solution by DNBC as manifested by weight gain, we have observed that in most cases the resulting DNBC-donor complexes are distinctly colored. The color of the complex depended on the particular donor being bound: pale yellow for DNBC-naphthalene to red-brown for DNBC-N,N-dimethylaniline (Table II). These color changes were clearly visible even when DNBC of low D.S. (less than 0.10) was used. The appearance of a broad new spectral band distinctly different from the composite spectra of the participating components is a characteristic feature of CT bonding. Therefore, the formation of color when DNBC is contacted by solutions of donors suggests that the observed adsorption phenomenon may result from a specific CT bond involving the 3,5-dinitrobenzoyl groups affixed to the cellulose and the π or n electron clouds of the various donors.

It was of interest to study the adsorption of donor by DNBC in further detail in one case. The percent weight gains observed when DNBC was treated with increasing concentrations of indole are tabulated in Table III along with the corresponding calculated f values. We have found that the binding of indole by DNBC is characterized by a single adsorption isotherm described by the following relationship

$$\frac{1}{f} = \frac{1}{nK(I)} + \frac{1}{n} \tag{1}$$

where f is the quantity defined above, n is the quotient of accessible sites to the total sites present per mole of DNBC, (I) is the indole concentration, and K is the equilibrium constant in M^{-1}. Equation (1) is a rearranged form of the classical Langmuir equation (10), which has found wide application in the study of the binding of small molecules by macromolecules (11,12). This relationship predicts that a plot of 1/f and 1/I gives a straight line whose intercept and slope equal 1/n and 1/nK, respectively. A plot of the data in accordance with eq. (1) is shown in Figure 1. The slope and intercept of this line were determined by the least squares method. From this plot K was evaluated as $1.2M^{-1}$ and n was found to be 0.75. Interestingly, this K value is very similar to the solution formation constant for the CT complex of indole and the p-nitrophenyl ester of 3,5-dinitrobenzoic acid in ethanol ($K = 1.4M^{-1}$) determined from Benesi-Hildebrand plots (13).

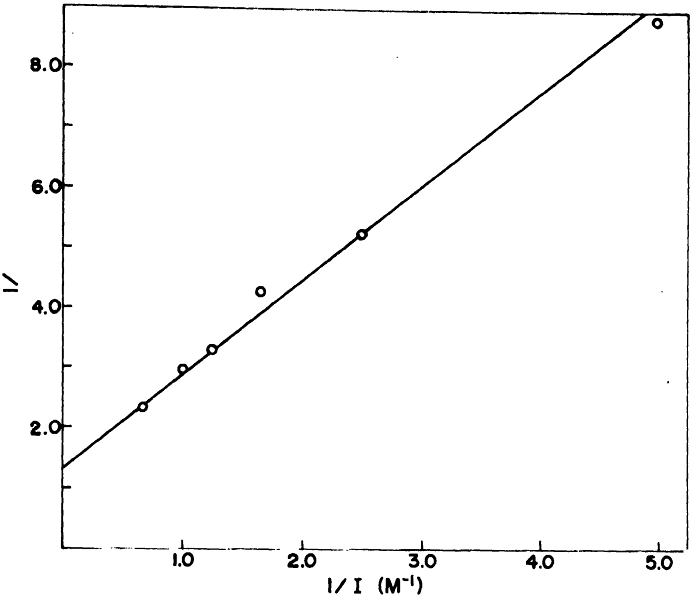

Fig. 1. Plot of 1/f versus 1/(Indole) for the determination of the binding constant (K) for the DNBC-Indole complex.

The method outlined provides a convenient means of quantitatively evaluating the intrinsic affinity of various monomers for DNBC. The relationship of K to monomer structure is currently under investigation with the hope that the specificity and mechanism of the binding of small molecules by DNBC can be elaborated in greater detail.

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Received June 13, 1973

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POLYMER LETTERS EDITION VOL. 11, PP. 701–704 (1973)

THE COLOR OF ABSORBING SCATTERING SUBSTRATES. II. THE PREDICTION OF THE COLOR OF A FIBER BUNDLE*

Introduction

Allen and Goldfinger (1) have shown the relationship between the color of a loose bundle of parallel cylindrical fibers and the optical properties of the constituent fibers. The validity of the treatment has been shown by predicting the effect of the ratio of the refractive indexes of the fibers and the continuous medium (2,3) and the effect of the distribution of the colorant in the fiber (4,5). In this note, some preliminary results are presented on the a priori prediction of the color of a parallel bundle of optically homogeneous fibers from two independently determined variables: the product of the coefficient of absorption of the dye in the fiber and its concentration and the refractive index of the fiber.

Experimental

"Vylor" nylon monofilament Type 0200 SA, 330 denier (.22 mm diameter) was dyed with disperse dyes, Sodyesperse Yellow G, and Sodyesperse Blue BN. Approximately 1000 meters of filament were loosely wound around a four-bladed paddle which was rotated in the dye bath. The paddles acted as turbin blades and assured a continuous vigorous flow of dye suspension around the filaments, giving uniform dyeing. After 24 to 30 hours of dyeing at 93°C, the sample was "soaped" for an hour at the same temperature in a solution containing a few drops of Triton X100.

In the treatment by Allen and Goldfinger, the two variables, coefficient of absorption and colorant concentration, appear as a product (CK). It was possible to determine this quantity by transmittance measurements through the fibers, minimizing the experimental error inherent in separate determinations. A fiber from the same lot, as used for the reflectance measurements, was wound around a frame so that adjacent fibers touched, providing a lightpath through two layers of those fibers. This frame was inserted into an absorption cell filled with monochlorobenzene (refractive index n_D = 1.524, compared to 1.52 – 1.57 for nylon) and measured against a cell containing only the liquid.

The refractive indexes of the system are sufficiently close to eliminate virtually any reflection and refraction at the fiber-liquid interface.

*This paper contains some of the results obtained by Lyn Stafford in fulfillment of the requirement of the course TC 490.

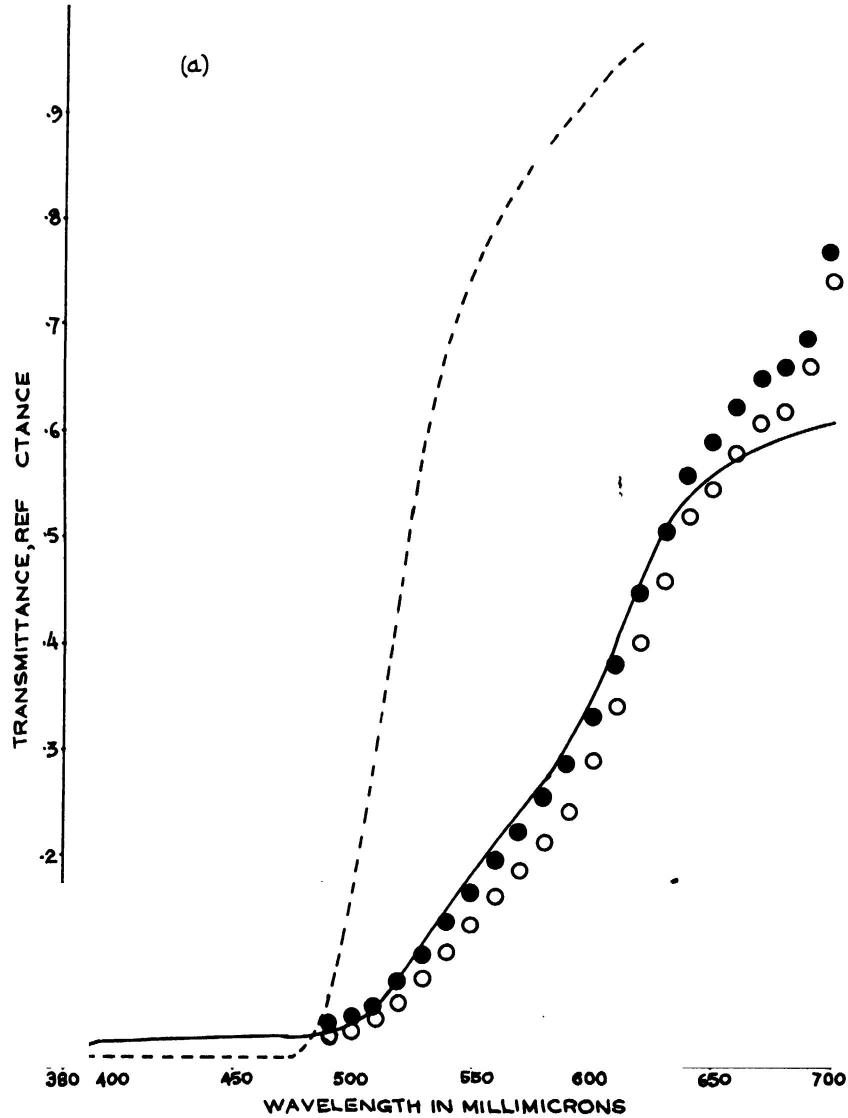

Fig. 1a

The length of the average lightpath through a cylinder can be easily shown to be $\pi r/2$. Thus through the two layers of fibers, it was πr.

Since in the Allen and Goldfinger treatment the coefficient of absorption was expressed in terms of fiber radius as the unit of length, from Beer-Lambert's law, under these experimental conditions

$$CK - \frac{\log_{10}\,(\text{transmittance})}{3}.$$

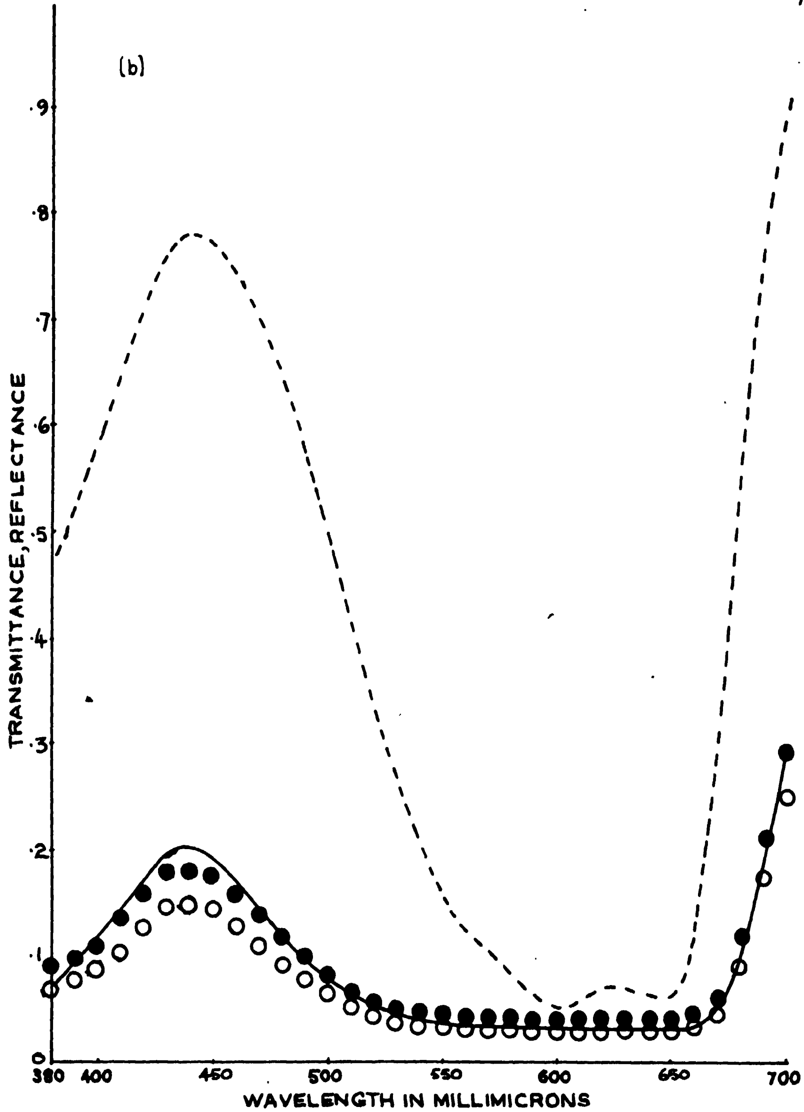

Fig. 1b

Fig. 1. Transmittance (–––), reflectance (——) and predicted reflectance (0 for n = 1.5 and for n = 1.6). a. Fiber dyed yellow; b. Fiber dyed blue.

For reflectance measurements, the fibers were wound with the help of a winding device which assured a parallel arrangement of the fibers onto a steel frame, forming 50 parallel layers.

The reflectance measurements were carried out against a standard of smoked magnesium oxide. The data reported are plots resulting from those

measurements. At this stage of the work it seemed unnecessary to correct for the minimal absorption of MgO in the 400 to 700 millimicron wavelength range.

Both the transmittance and reflectance measurements were carried out on a Hardy Spectrophotometer.

Results

The Allen and Goldfinger treatment expresses the reflectance of a loose, parallel bundle of fibers for any given refractive index ratio between fibers and the continuous medium in terms of a quantity CK: coefficient of absorption of the dye X dye concentration X fiber radius.

The quantity CK was determined at 10 millimicron intervals in the spectral range of finite transmittance from the data displayed on a tristimulus integrator. From these the reflectance was predicted for n = 1.5 and n = 1.6 using plots of reflectance against CK similar to the one shown in Figure 6 reference 1. Results are presented for two sets of dyeings (Figures 1a and 1b).

Conclusions

The authors have shown that the color of absorbing scattering substrates can indeed be predicted from the optical properties of the fibers without recourse to sample dyeings.

The authors wish to thank the E. I. duPont de Nemours and Company for the nylon filament and the Sodyeco Division of Martin Marietta Chemicals for the dyes.

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THE THERMAL STABILIZATION OF POLY(VINYL CHLORIDE) BY ALLYL XANTHATE SUBSTITUTION

Synopsis

The reaction of PVC with potassium allyl xanthate in DMF is discussed. Thermogravimetric analysis and differential scanning of calorimetry were used to evaluate the thermal stability. The allyl xanthate-modified PVC (AX-PVC) was shown to be significantly more thermally stable than the unmodified PVC homopolymer. The AX-PVC is completely crosslinked at temperatures > 180°C. It was found that dibutyltin di-2-ethylhexanoate, a commercial PVC stabilizer, does not produce the same effect on the thermal stability of the AX-PVC as it did on the unmodified PVC homopolymer.

Introduction

The inability to modify poly(vinyl chloride) (PVC) via nucleophilic substitution reactions without extensive degradation (competing β-elimination reactions) is well documented. However, in recent years, a number of publications have reported on the successful chemical modification of PVC without the occurrence of any significant degradation (1-10). Y. Nakamura reported on an investigation of the crosslinkability in ethylenediamine of PVC's modified by reaction with alkali xanthates; however, no comment was made on the heat stability of the modified polymers (4). In our laboratory, we have also been investigating the chemical modification of PVC with special interest in obtaining modified PVC's with increased heat stability. This communication is a report on our work in this area and provides information on a PVC with increased heat stability as a result of modification by reaction with potassium allyl xanthate.

Experimental

A commercial PVC (Diamond 450, $\overline{M}_n$ = 47,700) was employed in all reactions. The reactions were carried out by adding a potassium allyl xanthate/DMF solution to a reaction flask immersed in a constant temperature oil bath containing a PVC/DMF solution. The reaction was carried out with stirring under a nitrogen atmosphere. The modified polymers were isolated by precipitation with a water/methanol (1:1) solution and then purified by the tetrahydrofuran–methanol reprecipitation method. The allyl xanthate-modified PVC, henceforth referred to as AX-PVC, discussed in this report was prepared by reacting 35 g potassium allyl xanthate/200 ml DMF with 20 g PVC/200 ml DMF at 75°C for 1.5 hr. The AX-PVC contained 45.6% Cl and 7.03% S

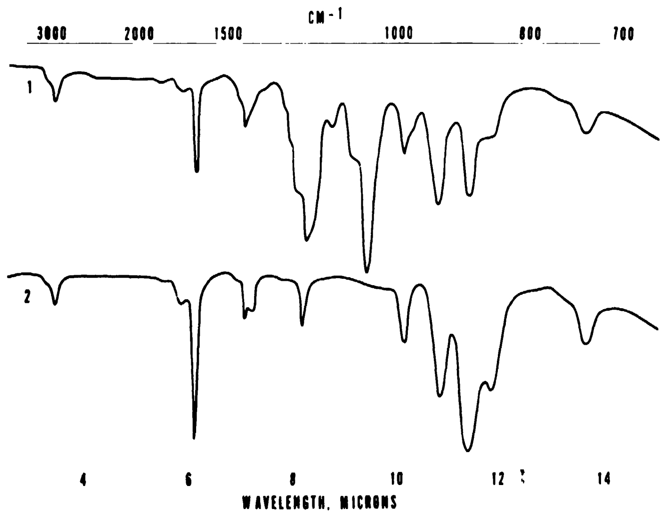


Fig. 1. Infrared spectra: 1. Product mixture from the potassium allyl xanthate/allyl bromide reaction; 2. Diallyl dithiolcarbonate.

(47.2% Cl and 7.1% S calculated for a PVC containing 7.7 mole % $-CH_2-CH-S-CS-O$ allyl$-$).

The infrared spectrum of the AX-PVC exhibits a characteristic absorption at 1050 cm^{-1} ($-O-CS-S-$, 1060-1070 cm^{-1}) (11). The ultraviolet spectrum exhibits a maximum absorption at 287 nm (methyl ethyl xanthate is reported to absorb at 280 nm) (12). More than 30 mole % of the CH_2CHCl groups in PVC can be substituted at high reaction temperatures and/or long reaction times. High conversions generally result in gelation or the production of cross-linked resins after work-up of the reaction.

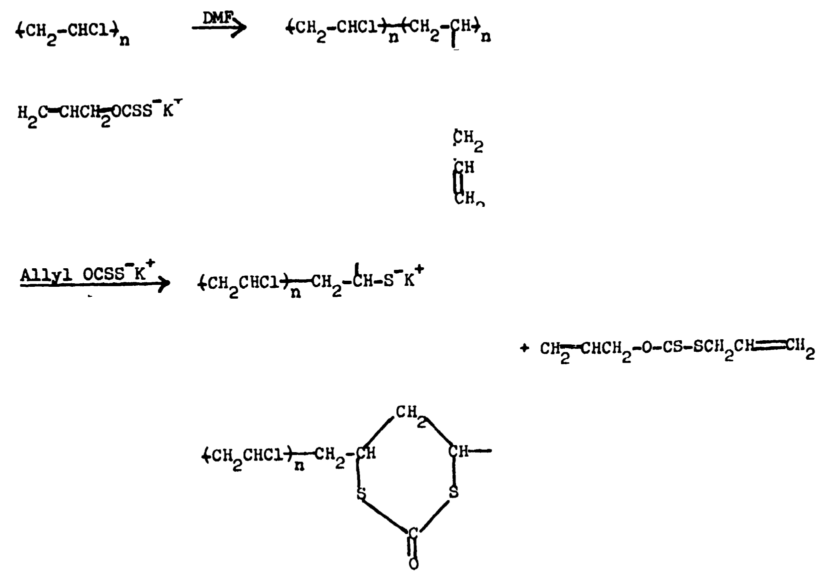
Two side products that have been identified as diallyl dithiolcarbonate and diallyl xanthate by comparison of their infrared and nmr spectra with the spectra of authentic samples were isolated from the PVC/potassium allyl xanthate reaction mixture. The infrared spectrum (Fig. 1) of the product mixture obtained from the reaction of potassium allyl xanthate (I) with allyl bromide (II) at 25°C and at 56°C indicate that essentially identical amounts of the xanthate (III) and dithiolcarbonate (IV) are produced. The infrared spectrum exhibits

$$\underset{\text{(I)}}{H_2C{=}CHCH_2{-}OCSS^-K^+} + \underset{\text{(II)}}{H_2C{=}CHCH_2Br} \xrightarrow{\text{acetone}}$$

$$\underset{\text{(III)}}{H_2C{=}CHCH_2{-}OCSS{-}CH_2CH{=}CH_2} + \underset{\text{(IV)}}{H_2C{=}CHCH_2{-}S{-}CO{-}SCH_2CH{=}CH_2}$$

strong absorptions for both the xanthate (1225 and 1070 cm^{-1}) and the dithiol-

carbonate (1648 and 880 cm^{-1}) groups. Only one product, the dithiolcarbonate, is obtained when the mixture is distilled at reduced pressure (1.5 mm/ 71-73°C). The production of diallyl dithiolcarbonate can be explained by the reasonable assumption (in view of the above observations) that diallyl xanthate is formed initially with the subsequent isomerization to the thermodynamically more stable dithiolcarbonate. There is spectral (infrared) evidence for the formation of the cyclic dithiolcarbonate structure (5) in some of the modified PVC's, particularly those that are highly substituted. All thermogravimetric and differential scanning calorimetry thermograms reported were obtained at 6 C/min in a nitrogen atmosphere. The thermogravimetric thermograms obtained in air were not significantly different from those obtained in nitrogen.



Results and Discussion

The AX-PVC resin is significantly more thermally stable than the unmodified PVC homopolymer. When the AX-PVC is pressed at 200°C under 25,000 psi pressure for one to three min, slightly yellowed films are obtained (the color of the bulk resin is a very pale yellow); on the other hand, pinkish-brown colored films are obtained when an unmodified PVC is subjected to identical conditions. The AX-PVC films obtained under the above conditions are completely crosslinked (determined by the insolubility of the films in (dsc) tetrahydrofuran, cyclohexanone, and dimethylformamide); the unmodified PVC sample yields no detectable crosslinked material.

Thermal gravimetric analysis (tga) and differential scanning calorimetry

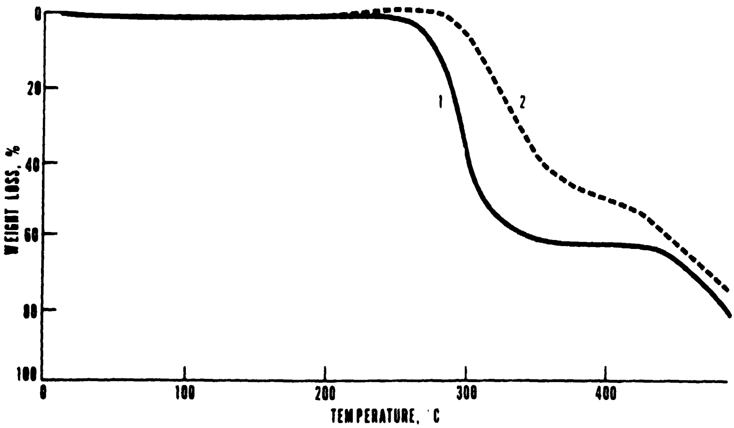


Fig. 2. TGA thermograms: 1. Unmodified PVC homopolymers; 2. AX-PVC.

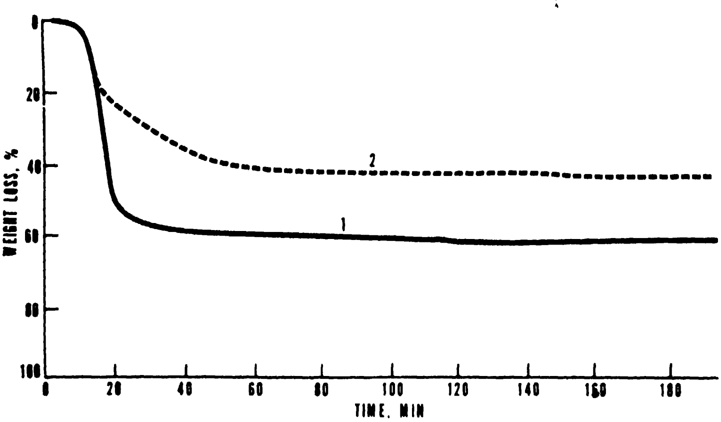


Fig. 3. TGA thermograms (275°C): 1. Unmodified PVC homopolymers; 2. AX-PVC.

were used extensively in the characterization of the thermal properties of the AX-PVC resins. In Figure 2, a tga thermogram of a PVC control is compared with that of the AX-PVC resin. Below 250°C, both polymers are of comparable stability; however, between 250 and 450°C, the AX-PVC is significantly more stable. A study of the thermal stability at 275°C as a function of time (see Fig. 3) further illustrates the increased thermal stability of the AX-PVC at higher temperatures (> 250°C). The PVC control underwent a 52% weight loss in 20 min and 60% in 60 min with no further weight loss occurring within the time period studied (180 min). In contrast, the AX-PVC underwent a 23% weight loss in 20 min and 40% in 60 min with no further weight loss occurring.

In Figure 4, the dsc thermograms of a PVC control and AX-PVC are compared. The slight change in the slope of the curves in the 75 to 85°C range can be attributed to the glass transition temperatures (Tg) of the PVC control

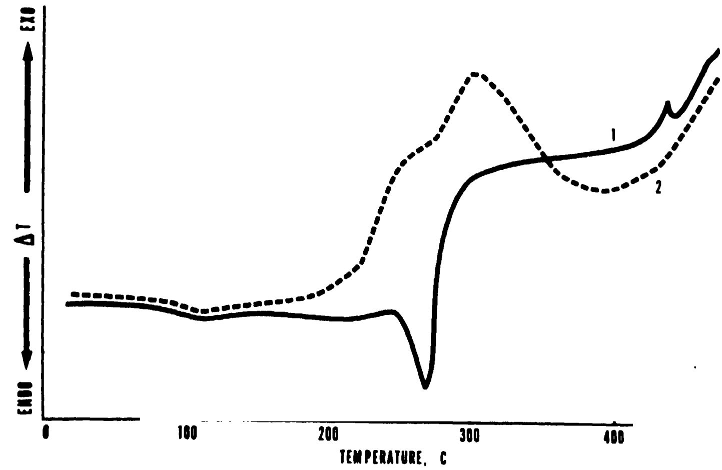


Fig. 4. DSC thermograms: 1. Unmodified PVC homopolymers; 2. AX-PVC.

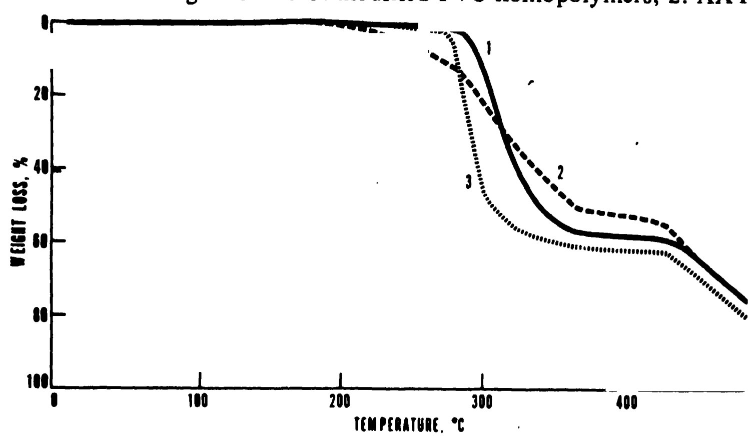


Fig. 5. TGA thermograms: 1. Unmodified PVC homopolymer/2phr DTD; 2. AX-PVC/2phr DTD; 3. Unmodified PVC homopolymer.

and AX-PVC which occur at 81 and 82°C, respectively (the Tg's, determined by dsc of AX-PVC resins in which 0.1–30 mole % of the CH_2CHCl groups were substituted, were essentially unchanged from that of the unmodified PVC). The dsc curves for the control and AX-PVC exhibit very pronounced differences between 200 and 350°C. The PVC control shows an endotherm with a peak minimum at 268°C which is primarily associated with the elimination of hydrogen chloride. The change in the baseline following the endotherm can be attributed to a change in the thermal properties of the sample. In contrast, the AX-PVC exhibits two broadened exotherms with peak maximums at 267 and 303°C. The AX-PVC is known to be readily crosslinked thermally (> 180°C); if the thermal effects of exothermic crosslinking reactions predominate over the endothermic hydrogen chloride elimination reaction

at 200 to 300°C, one might expect an exothermic peak(s) to appear in this temperature range as was observed.

In Figure 5 are shown tga thermograms for a PVC control and AX-PVC to which have been added 2 phr dibutyltin di-2-ethylhexanoate (DTD), a commercial PVC stabilizer. From this figure, it can be seen that the DTD did not produce the same effect on the thermal stability of the AX-PVC as it did on the control.

The precise mechanism of the stabilization reaction is not known; however, it has been demonstrated from studies on styrene–trivinylbenzene copolymers that the thermal stability varies with crosslink density (13). Thus, it is logical to assume that the mechanism of stabilization is controlled by the thermal decomposition mechanism of the allyl xanthate group (or other modified structures that may have been introduced via the xanthate reaction), which presumably controls the crosslinking reaction.

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Received July 31, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 711–715 (1973)

EFFECT OF ACID ON THE RADIATION-INDUCED COPOLYMERIZATION OF MONOMERS TO CELLULOSE

Extensive work has already been reported for the radiation-induced copolymerization of monomers to cellulose (1-4). In particular, it has been found that for a particular monomer in a particular solvent, a peak in the grafting yield versus composition curve can be observed at a given dose and dose-rate (3). This Trommsdorff effect occurs at approximately 30% vol/vol styrene in methanol for cellulose, the position of the peak varying with the structure of monomer and solvent, whilst the magnitude of the effect is also dose and dose-rate dependent.

TABLE I

Effect of Sulfuric Acid on Radiation Grafting of Styrene in Methanol to Cellulose[a]

Styrene (%) in MeOH	Graft (%) in concentration of sulfuric acid (molarity)							
	0.0[b]	1.1×10^{-3}	5.4×10^{-3}	1.1×10^{-2}	5.4×10^{-2}	1.1×10^{-1}	5.4×10^{-1}	1.1
10	1.2	5.4	15.1	7.5	8.8	11.0	19.4	21.2
20	8.9	22.6	28.6	28.7	38.4	48.2	58.5	74.7
30	13.9	41.0	lost	44.7	47.5	49.6	39.3	27.0
40	16.3	27.5	37.1	17.8	34.0	30.2	20.2	16.1
60	29.8	31.2	28.0	29.1	26.8	23.0	16.5	15.1
80	34.1	24.8	21.7	26.5	19.3	21.3	12.4*	10.1

[a]Irradiation in vacuum, at a dose rate of 2.73×10^4 rad/hr to a total dose of 0.2×10^6 rad.

[b]Note no Trommsdorff peak present without acid, but inclusion of acid induces peak.

We have now found that if certain mineral acids are added to the styrene solution in methanol prior to irradiation, accelerated grafting is observed during the copolymerization reaction (Table I). Thus in Table I there is a progressive increase in graft for the 10% monomer solution from 1.2% (no acid) to 21.2% (1.1 MH_2SO_4). With the 20% solution, the corresponding increase in graft is from 8.9 to 74.7%. Furthermore, under the radiation conditions used in Table I, there is no Trommsdorff peak without acid. Inclusion of acid (at

TABLE II

Effect of Acid on Trommsdorff Peak in Radiation Grafting of Styrene to Cellulose[a]

Styrene (%) in MeOH	Graft (%) in concentration of sulfuric acid				
	0.0M[b]	$.9\times10^{-4}$M	$.9\times10^{-3}$M	$.9\times10^{-2}$M	$.7\times10^{-1}$
15	35.1	38.4	31.5	50.8	78.7
20	61.9	69.3	65.6	87.2	109.8
25	99.3	112.5	110.8	123.3	162.7
30	104.5	113.9	98.8	109.6	v. high
35	100.9	102.8	80.0	90.7	124.0
45	80.5	52.6	42.0	48.4	82.5

[a]Irradiation in vacuum at a dose rate of 6.77×10^3 rad/hr to a total dose of 0.12×10^6 rads.

[b]Note Trommsdorff peak present without acid and inclusion of acid accentuates the peak.

all concentrations studied) not only induces the Trommsdorff effect, but also the position of the peak progressively changes from 30% monomer in solvent (1.1×10^{-3}M H_2SO_4) to 20% (1.1 M H_2SO_4).

If the dose rate is lowered for the styrene-methanol system from 2.73×10^4 rad/hr (Table I) to 6.77×10^3 rad/hr (Table II) for the same total dose, there is a corresponding increase in graft as previously reported (3). Under the new radiolysis conditions in Table II, a Trommsdorff peak is now observed with no acid present, again consistent with published data (3). However, when acid is added to this system the intensity of the Trommsdorff peak is increased and tends to move from 30% to lower monomer concentration as the acid concentration is increased. Thus, acid can (a) induce a Trommsdorff effect in the current system or (b) enhance the magnitude of the effect if it is already present.

The above trends in data are more clearly evident if the data are graphed (Figs. 1 and 2). The magnitude of the acid effect is decreased in the presence of air. Of all monomers studied to date, styrene gives the most significant acid-induced radiation effects. Sulfuric is the most reactive of the mineral acids.

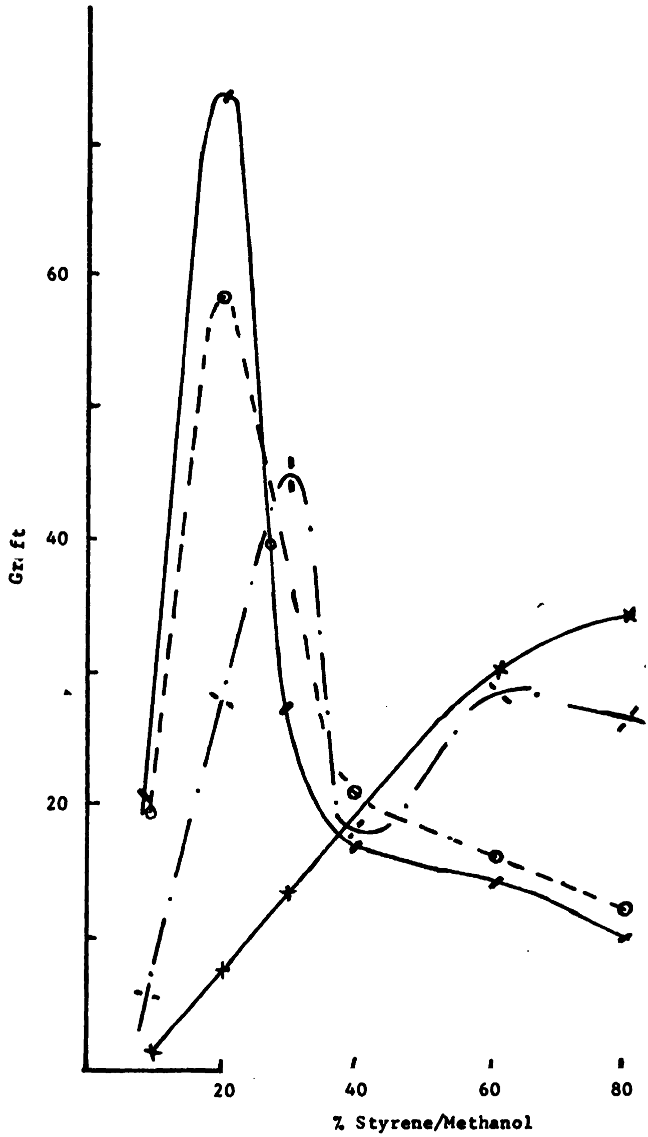

Fig. 1. Induced Trommsdorff peak in presence of acid for radiation grafting of styrene to cellulose (radiation conditions as in Table I). —x—x—x— is 0.0M H_2SO_4; —″—″—″— is 1.1 × 10^{-2}M H_2SO_4: —o—o—o— is 5.4 × 10^{-1}M H_2SO_4; and —■—■—■— is 1.1M H_2SO_4.

The present acid effect in radiation copolymerization may be related to general acid effects observed in the radiation chemistry of simple molecules such as methanol (5-7). In the radiolysis of methanol, addition of acid increases the $G(H_2)$ yield, presumably by increasing G(H) through interaction of the

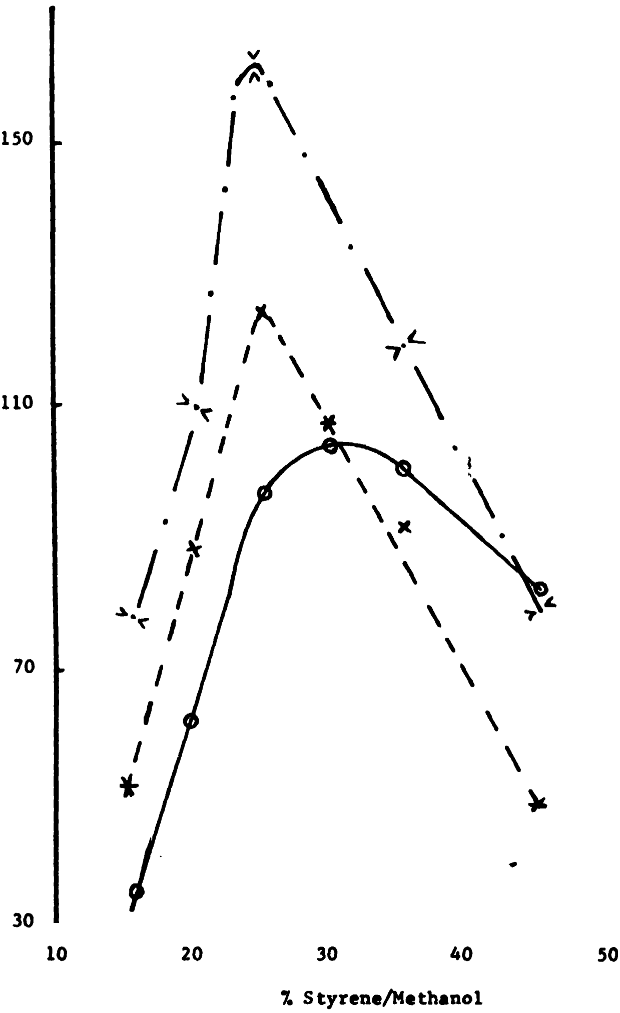

Fig. 2. Enhanced Trommsdorff peak in presence of acid for radiation grafting of styrene to cellulose (radiation conditions as in Table II). —o—o—o— is 0.0M H_2SO_4; —x—x—x— is 0.9 X 10^{-2}M H_2SO_4; and —$\frac{V}{\Lambda}$—$\frac{V}{\Lambda}$—$\frac{V}{\Lambda}$— is 0.7 X 10^{-1}M H_2SO_4.

secondary electrons from the radiolysis with the H^+ from the mineral acid (eq. 1).

$$CH_3OH_2^+ + e \longrightarrow CH_3OH + H \tag{1}$$

Further support for this interpretation of the acid grafting effect is that data are accumulating (7) which suggest that the Trommsdorff peak in radia-

tion grafting (no acid) is due to H atom scavenging. Thus the addition of any component which will increase G(H) in the grafting system should also affect the appearance of the Trommsdorff peak in a positive manner. The work is at present being extended to other trunk polymers.

We thank the Australian Institute of Nuclear Science and Engineering and the Australian Atomic Energy Commission for the irradiations. We are also grateful to the Australian Research Grants Committee and the Australian Wool Corporation for continued support.

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Received August 28, 1973

VISCOSITY OF LINEAR AND BRANCHED POLYMERS IN CONCENTRATED SOLUTIONS AND MELT

The zero-shear, isobaric viscosity of polymer solution, η, depends on solvent viscosity, η_0, temperature, T, concentration, c, polymer-solvent interactions parameter, B, polymer molecular weight, M, polydispersity factor, M_w/M_n, and branching parameter, g. For linear polymers (g = 1) the existance of the Principle of Corresponding States, PCS, was demonstrated (1-6) to hold for sixteen polymer-solvent systems in a wide range of variables η_0, T, c, M, M_w/M_n and B. A summary of the method was published recently (7).

The influence of polymer structure on the applicability of PCS was also analyzed (8). In the study, well characterized samples of anionic, linear, 4- and 6- star branched polystyrenes, PS, were used. Polymers were dissolved in di(ethyl)benzene. The c = 25.5 (g/cm^3) solutions were measured at 30.0°C using cone-and-plate and capillary rheometers. The data were used to test the applicability of all the main theoretical and/or semi theoretical dependencies for polymer solution viscosity. On the basis of this analysis, it was concluded that only PCS allows one to reduce the three sets of data (these of linear, 4- and 6- branched PS solutions) into one master dependence in the whole range of investigated parameters.

This observation not only improves our understanding of the flow behavior of macromolecules, but also has a very practical application; it allows one to compute the high concentration viscosity of star branched PS from the numerical values of η of the linear PS and from g, or intrinsic viscosity, $[\eta]_\theta$, (the subscript θ indicates the B = 0 conditions) of the branched polymer. The question still remains if PCS is valid for other type of branched macromolecules than the model star-branched samples, and if the validity extends over the whole concentration range.

Recently Pannell (9) reported melt viscosity and $[\eta]$ data for linear PS and for the mixtures of linear and comb-branched PS containing from 17.8 to 100 w/w of the branched material. As the $[\eta]$'s were measured near θ-condition (cyclohexane, CH, 35.0°C) and in a relatively good solvent (tetrahydrofurane, THF, 25.0°C) the data can be used to test the applicability of PCS to comb-branched system.

For polymer melts, PCS predicts that the plot $\eta/[\eta]_\theta$ vs $[\eta]_\theta$ should reduce the data into a single "master dependence". Such a plot is shown in Figure 1 on the lower curve. It can be seen that the superposition of linear and comb-branched polymers is indeed obtained. The scatter of the data points is large, but random. The solid line was computed by the least-squares method using only the data above the critical entanglement molecular weight $M_c > 7 \times 10^4$. The following dependence was assumed:

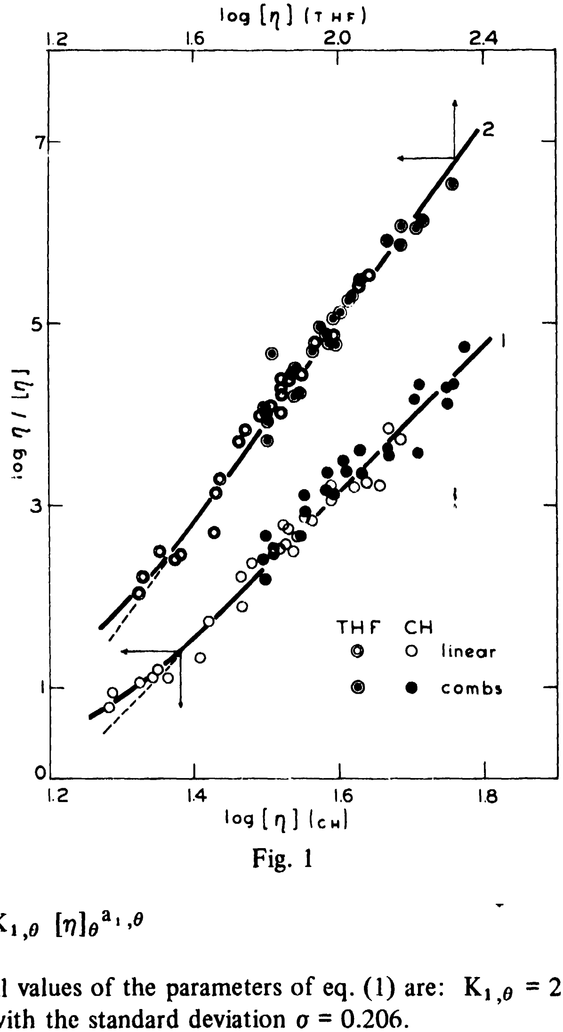

Fig. 1

$$\eta/[\eta]_\theta = K_{1,\theta}\ [\eta]_\theta^{a_{1,\theta}} \tag{1}$$

The numerical values of the parameters of eq. (1) are: $K_{1,\theta} = 2 \times 10^{-10}$, $a_{1,\theta} = 8.03$ with the standard deviation $\sigma = 0.206$.

In Figure 1, the upper set of data was computed using the same melt viscosities, η, and the intrinsic viscosities determined in THF, $[\eta]$(THF). Also, in this case a good superposition is obtained. The computed values of the parameters K_1 and a_1, of an analogous relation to that of eq. (1), but written for non-θ-conditions, are: $K_1 = 1.1 \times 10^{-6}$ and $a_1 = 5.48$. The scatter of the data points for the upper set in Figure 1 is smaller than that for the lower set, which is reflected in the smaller value of the standard deviation: $\sigma = 0.182$. This difference in the standard deviation is a result of greater experimental difficulties in measuring the intrinsic viscosity in CH than in THF. This can be easily demonstrated for the linear PS samples, for which both $[\eta]$'s and the number average molecular weights, M_n, are known. The parameters of the Mark-Houwink-Sakurada equation,

$$[\eta] = KM_n^a \tag{2}$$

are as follows: K(CH) = 0.169, a (CH) = 0.443, σ (CH) = 0.209 and K(THF) = 0.0209, a (THF) = 0.673, σ (THF) = 0.169. One can expect that the analogous dependencies for nonlinear systems will show even larger variations in σ.

The value of a (CH) $<$ ½ is in variance with the other reported data for the system (10). It indicates that under the experimental conditions employed by the author (9), $\theta > 35.0°C$ for linear PS in CH. On the other hand the lowering of θ with the degree of branching was demonstrated (11) both experimentally and theoretically. Consequently, the $[\eta]$ (CH)'s represent different thermodynamical conditions for each degree of branching. This divergence may gradually disappear with the improvement of the solvent.

The applicability of PCS to branched polymer solution can strictly be tested if the $[\eta]_\theta$'s determined under B = 0 conditions are known. In the absence of such information, the present results may indicate the applicability of PCS, but can not be taken as a proof. The difference in reliability of $[\eta]$'s determined in CH and in THF further overshadows the true correlation. Consequently, the superposition of the viscosity data on a "master curve", obtained at and above the critical entanglement region for star-branched (8) and comb-branched polystyrenes, may indicate the generality of the method, at least within the tested entanglement region. However, before a more rigorous test is conducted, it should be treated as a semi-empirical correlation, which can be of value to these experimenting with polymers of variable branching type and density.

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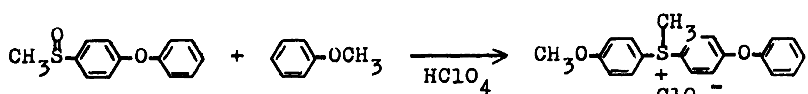
Received July 31, 1973

PREPARATION OF POLY(ALKYL- AND ARYL-p-PHENOXYPHENYLSULFONIUM SALTS)

Recently much interest has been attracted to onium polymers, but the studies were almost confined to ammonium polymers (1). Few reports which deal with the preparation of linear sulfonium polymers include only trialkylsulfonium polymers (2), which are generally so unstable as decomposing at room temperature.

We wish to report here the synthesis of new linear poly(alkyl- and aryl-p-phenoxyphenylsulfonium salts), which are more stable than trialkylsulfonium polymers. As the preparation of aromatic sulfonium compounds of low molecular weight is well known (3), attempts were made to prepare the sulfonium polymers by self-polycondensation of alkylsulfinyl- and arylsulfinylphenoxybenzene in a mixture of 70% perchloric acid (PA) and phosphorus oxychloride (PO).

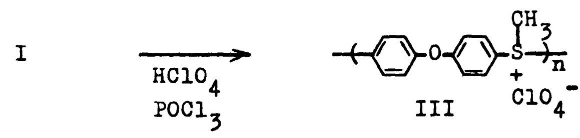
As a model reaction of polycondensation, the reaction of p-methylsulfinylphenoxybenzene* (I, mp 42 ~ 44°C) with anisole was examined. When the reaction of I (23.2 g) with anisole (40 ml) was carried out in 80 ml PA-PO (5:4 mixture by volume) at room temperature, methyl-p-anisyl-p-phenoxyphenylsulfonium perchlorate (II) was isolated in a 88% yield. The NMR and the infrared spectra indicated the presence of two p-substituted phenylene groups. This result showed that I was selectively introduced to the para-position of anisole.



I II

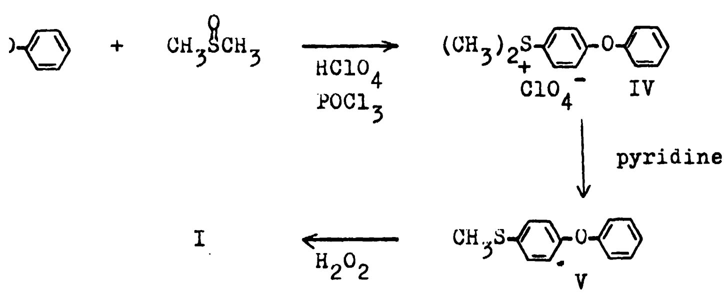
Further development of this highly selective and mild sulfonium synthesis was directed to self-polycondensation of I. The polymerization of I (0.02 mole) was carried out in PA-PO (36 ml) under an argon atmosphere at room temperature for 20 hr and then at 50 ~ 60°C for 6 hr. The resulting reaction mixture was poured into cold water to give a brittle polymer, as a white amorphous solid, in a quantitative yield; dec.p. 203°C; η red = 0.27 (1% solution) and 0.30 (0.1% solution) in HCOOH at 30°C; NMR (in $CDCl_3$) δ 3.78 (s, 3H), 7.43 (d, 4H), 8.33 (d, 4H); infrared (KBr disc) 1080, 624 cm^{-1}; Anal. found: C, 49.48; H, 3.62; Cl, 11.08; S, 10.10%. Calcd. for $C_{13}H_{11}ClO_5S$: C, 49.61; H, 3.52; Cl, 11.26; S, 10.19%. The structure of the polymer was

*All new compounds in this letter have given suitable NMR and infrared spectra, and elemental analysis.



confirmed to be poly(methyl-p-phenoxyphenylsulfonium perchlorate) (III) by the NMR spectrum which showed a sharp AB quartet due to aromatic protons, indicating that the polymer consists of phenylene groups with para-position linkage. The sulfonium polymer was insoluble in water, and soluble in formic acid and aprotic polar solvents.

The starting material I was prepared by the oxidation of p-methylthiophenoxybenzene (V). Although V has been prepared from sodium p-mercaptophenoxybenzene and methyl iodide (4), the following procedure was found to give more satisfactory results. Dimethyl-p-phenoxyphenylsulfonium perchlo-



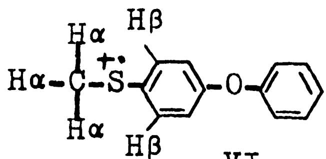
rate (IV, mp 139 ~ 141°C) was prepared by the reaction of diphenyl ether (85 g) with dimethyl sulfoxide in PA-PO (180 ml) at room temperature. The compound IV was dealkylated in boiling pyridine to give V in a 76% yield (from diphenyl ether). The oxidation of V by 30% hydrogen peroxide in acetone at room temperature afforded I in a 70% yield.

It is noteworthy that the sulfonium polymer III was also obtained in a 90% yield by the polymerization of the sulfide V in the presence of an equimolar amount of hydrogen peroxide (30%) in PA-PO; dec.p. 181°C; η red = 0.11 (1% in HCOOH at 30°C).

In a similar way, the polymerization was tried for some p-alkylsulfinyl- and p-arylsulfinylphenoxybenzenes. p-Ethylsulfinylphenoxybenzene gave poly(ethyl-p-phenoxyphenylsulfonium perchlorate): dec.p. 165°C; η red = 0.55 (1% in HCOOH at 30°C). p-Anisyl-p-phenoxyphenyl sulfoxide afforded the corresponding triarylsulfonium polymer: dec.p. 275°C; η red = 0.06 (1% in HCOOH at 30°C).

The ESR spectra of I in PA-PO showed 12 lines (g = 2.0077, $a_{H\alpha}$ = 8.2G,

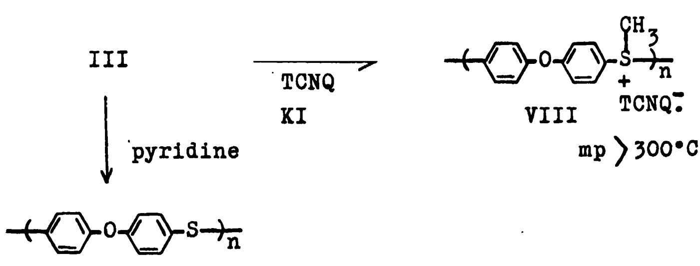
$a_{H\beta}$ = 2.7G) which indicated that the polymerization reaction might proceed through a radical cation intermediate as VI. Owing to the consumption of the radical cation by free oxygen, the polymerization could not proceed smoothly in air and the yield and viscosity of the polymer were low.



VI

The polymer III was dealkylated on treatment with boiling pyridine for 12 hr to give poly(p-phenoxyphenyl sulfide) (VII, mp 188°C, η red = 0.27 (1% in HMPA at 30°C)) in an 80% yield. The dealkylated polymer showed exactly identical infrared and NMR spectra with those of an authentic sample prepared by the reaction of diphenyl ether with sulfur chlorides in the presence of a small amount of iron powder (5).

Furthermore, the electrically conducting polymer, VIII, was obtained by treating the sulfonium polymer III with an equimolar amount of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in the presence of potassium iodide in acetonitrile. The electrical resistivity of the TCNQ salt polymer was 8.3 X 10^6 ohm•cm.



Linear polymers with sulfonium groups in the main chain reported so far have been prepared only by alkylation of poly(alkylene sulfide). The present method, which enables direct synthesis of sulfonium polymers from low molecules, would afford a wide application for the preparation of arylenesulfonium polymers.

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Received August 6, 1973
Revised September 13, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 725–729 (1973)

PSEUDO-RAMAN BEHAVIOR OF THE SCATTERING BROAD BAND OF BSA

A broad band obtained from Bovine Serum Albumin in powder form, with different exciting laser lines, cannot be explained by a fluorescence approach. Data provide evidence for the pseudo-Raman nature of this broad band.

With the advent of the laser, especially ion lasers, there is a renaissance of Raman spectroscopy. Since it provides molecular information, attempts are made to extend it to the investigation of long polymers. The Raman spectra of those samples, especially in solid or powder form, exhibit a very large broad band which makes difficult, and at times impossible, the determination of molecular Raman lines. In some cases the broad band is simply a fluorescence, easily identifiable as due to the sample itself or added impurities.

There is a tendency to assume that those broad bands are always due to fluorescence, even when they have some unusual behavior. For example, some of them decay with laser exposure. It is even common practice, among Raman spectroscopists, to destroy such a broad band by exposure of the sample at high laser power before recording the Raman lines. Such a broad band is of considerable interest, and instead of being destroyed, deserves a careful investigation. We have performed such investigation for several organic, inorganic, and biological high polymers, and found that their spectrum is not a fluorescence. Such is the case for Bovine Serum Albumin (BSA); the data are presented here as a prime example. They cannot be explained by a fluorescence theory, but clearly show a pseudo-Raman behavior.

The Raman lines and the nonfluorescent broad band obtained in long polymer chains are two different phenomena. One can still record individual Raman lines superimposed on a medium intensity broad band as demonstrated for BSA (1) and Human Serum Albumin (2) (HSA). The recording of those Raman lines had to be done with laser input power in the milliwatt range, instead of one watt available from the laser, in order to preserve the broad band. It is well known that exposure of chain molecules to large laser intensities reduces, distorts, and even destroys (3) the nonfluorescent broad band. Bellocq et al. could not record the normal Raman lines of BSA without destroying first the background broad band. After such a destruction it is very easy to record the Raman lines, especially at a watt laser power. This alone is a proof that this broad band is not of the same nature as the normal Raman lines and that it is not made up by their sum since they would have disappeared during the laser treatment together with the broad band. This makes also clear that the latter is not due to some impurities which should remain active during and despite the laser treatment. Another observation that can be made from the

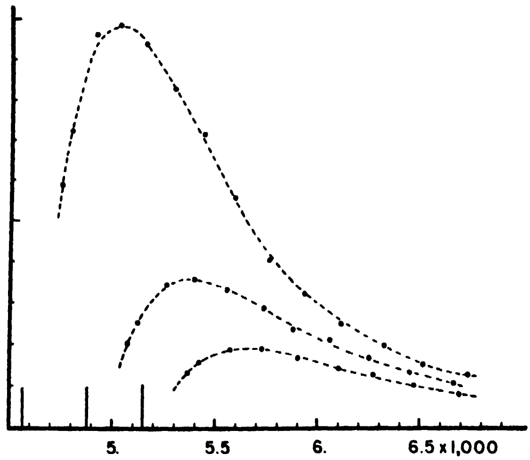

Fig. 1. Broad bands from powder BSA obtained at three exciting laser lines. Left spectrum: laser 4579 Å; middle spectrum: laser 4880 Å; right spectrum: laser 5145 Å; and laser power: 1 mw.

previous data (1,2) is that the broad band is at its top an order of magnitude larger than the Raman lines. It is not unusual to find that in many molecules the intensity of the broad band exceeds by two orders of magnitude that of the Raman lines of the same molecule.

One has also to report that those nonfluorescent broad bands decay rapidly by building a water layer around the molecules. Still more important, if one decomposes the molecular chain in its amino acid components, the broad band disappears. The short length components of the chain by themselves, and impurities if any, do not produce the original spectrum. In addition, the peak of the pseudo-Raman band of BSA suspended in water was reported in a sketch (4) around 3000 cm^{-1}. When BSA is in powder form, the peak of the same band moves to around 2000 cm^{-1}, while the intensity grows. If one increases further the intermolecular couplings, this peak shifts down to 1000 cm^{-1} or even below. All these specific behaviors of those broad bands, produced by chain molecules, cannot be understood in terms of fluorescence.

We are presenting here additional data obtained in high purity BSA, in dry powder form, that substantiates the same argument. In order to minimize the perturbation of the molecules and obtain reliable data of the broad band only, one milliwatt of unfocused laser input was used on the sample. The counting time was 1 sec and the laser beam was interrupted for 29 sec, providing the time for the molecules to reestablish disturbed intermolecular couplings. The resolution of the monochromator was reduced to $\cong$ 100 cm^{-1} in order to average the normal Raman lines and thus minimize their contribution to the profile of the broad band which is solely desired in the present investigation.

We compensate for the low scattering intensity by using F matched, large

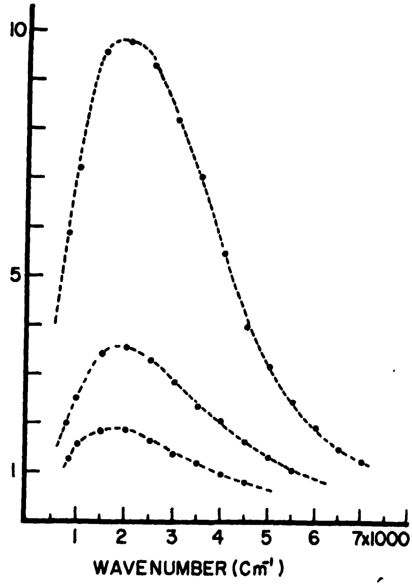

Fig. 2. The same data points as in Figure 1 are plotted in a Raman scale; the three broad bands are superposed: this indicates a pseudo-Raman phenomenon. Top spectrum: laser 4579 Å; middle spectrum: laser 4880 Å; and lowest spectrum: laser 5145 Å.

aperture monochromator. For additional brightness, the second monochromator is replaced by filters attenuating the laser line by six orders of magnitude while passing 80% of the spectrum between 600 and 8000 cm^{-1}. A GaAsP photocathode photomultiplier, selected for maximum S/N, is followed by an SSR 1110 + 1120 photon counting system. All the data presented here are corrected for instrumental parameters: filters, grating blaze, and photocathode quantum efficiency. This way the curves of Figures 1 and 2 show the real profile of the investigated broad band.

The scattering data obtained at 4579, 4880, and 5145 Å, versus monochromator wavelength, are displayed in Figure 1. Two observations can be immediately made from this figure. (A) The broad bands obtained for all three exciting wavelengths start with zero counts close to the exciting line. This would not be the case if the exciting line was within a real fluorescence band, and possibly close to its peak. (B) The broad band obtained with the 4579 Å line lies to the left of that obtained with the 4880 Å line and that one to the left of the broad band obtained with the 5145 Å exciting line. It is clear that this broad band does not behave as a classical fluorescence. The shift of its peak, in the same direction as the exciting line, suggests a Raman-like behavior.

If one calculates the frequency differences between the exciting line and the peak of each broad band, one obtains the same number for all three cases! The results of subtracting the frequency of each data point from the respective

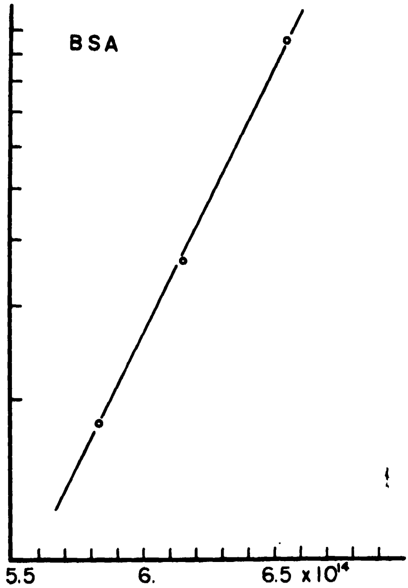

Fig. 3. Semi-log plot of the photon counting rate at the peak of the broad band versus laser frequency.

exciting frequency are presented in Figure 2 in cm^{-1} scale. The superposition in Raman scale (superposition is impossible in fluorescence scale) of the data obtained at three different laser lines shows that the broad band of BSA, which is not the sum of the normal Raman lines, has in turn a pseudo-Raman behavior. The superposition is not absolutely exact, since there could be a small hump to the right of the peak of the top spectrum of Figure 2 and to the left of the peak of the bottom spectrum, due to a secondary phenomenon, but hardly visible here. The contribution of this secondary phenomenon to the broad band increases as the latter is dampened by water layers around the molecules (especially in shorter chain molecules). It is thus very important, in order to obtain well superposed pseudo-Raman bands, to use dry lyophilized BSA samples.

In Figure 2 we can also note a Raman-like susceptibility decrease with increasing exciting wavelength. By plotting in a semi-log scale, as in Figure 3, the photon counting rate at the peak of each pseudo-Raman band versus exciting laser frequency, an exponential variation is found. It is a characteristic feature of this type of broad band and not of conventional Raman ($\alpha\nu^4$) to give an exponential dependence versus frequency.

One could list here some of the specific features of the nonfluorescent bands of long chain molecules: 1. The broad band disappears when the chain is destroyed; 2. The broad band has a pseudo-Raman behavior (not easy to show for all chains); 3. Water layers around the molecules dampen vastly the

broad band; 4. Water (and other compounds) shift down in frequency the wide peaks into which the broad band can be resolved (5); 5. The broad band decays, or gets distorted, by excessive laser input. That is why we use the minimum possible input power. 6. The intensity, at the peak of the broad band, shows an exponential variation versus laser frequency; and 7. In cm^{-1} scale the broad band is asymmetrical and extends beyond 6000 cm^{-1}.

One would have to account for all of those specific behaviors. In our systematic investigation of these pseudo-Raman bands (in PGA, BSA, HSA, ESA, Ovuline Albumin, β-lactoglobulin, and several viral DNA's), we have been able to resolve them by a special technique (5) in a series of wide peaks. These series of pseudo-Raman wide peaks explain the asymmetrical shape, the extension beyond 6000 cm^{-1}, and other features specific to these nonfluorescent broad bands. Furthermore, the position of those resolved wide peaks is directly related to the chain length (6).

A similar pseudo-Raman band has been observed in Poly-L-Glutamic acid of 93,000 molecular weight (7).

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Received July 25, 1973
Revised September 25, 1973

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Polymer Letters Edition

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Journal of Polymer Science: Polymer Letters Edition

The *Journal of Polymer Science* is published as follows: *Polymer Chemistry Edition,* monthly; *Polymer Physics Edition,* monthly; *Polymer Letters Edition,* monthly; *Polymer Symposia,* irregular.

Published monthly by John Wiley & Sons, Inc., covering one volume annually. Publication, Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, New York 10016. Second-class postage paid at New York, New York and additional mailing offices. Subscription price, $350.00 per volume (including *Polymer Chemistry Edition, Polymer Physics Edition* and *Polymer Symposia*). Foreign postage $18.00 per volume.

POLYMER LETTERS EDITION VOL. 11, PP. 731-735 (1973)

A NEW CLASS OF BIODEGRADABLE POLYMERS

Introduction

Block copolymers have become of considerable interest in recent years because of their many unique properties. A comprehensive review of the whole field has recently been published (1). Among the many methods of synthesis, the use of diisocyanates as coupling agents for polymeric diols and other difunctional polymers has been extensively investigated (2). Steinman (3,4) has extended this method to cellulosic blocks using cellulose triacetate oligomeric species having hydroxyl end-groups which are capable of reacting with polyester, polyether, or other polymers containing hydroxyl or other functional end-groups by coupling with organic diisocyanates. Such copolymers are interesting because of their novel properties, for example, Steinman has prepared elastomeric fibers from his block copolymers. Removal of the hydroxyl blocking acetyl groups on the cellulose triacetate blocks gives rise to another group of block copolymers. It was thought that such an approach would lead to bio degradable polymers. It is the purpose of this communication to demonstrate that this is, indeed, a feasible approach to preparing biodegradable polymers with a wide variety of properties depending on the composition of the block copolymers.

Other properties of this class of block copolymers are currently being studied in these laboratories and these will be the subject of a future communication.

Experimental

Depolymerization of Cellulose Triacetate

Cellulose triacetate (acetyl value – 43.9%; $[\eta]$ = 1.77 dl/g in 9/1 CH_2Cl_2/CH_3OH) was depolymerized in 99.4% acetic acid solution following the procedure of Steinmann (3), but the time of hydrolysis was 6 hr. Yield, 93%; $[\eta]$ = 0.16 dl/g in 9/1 CH_2Cl_2/CH_3OH); acetyl value 45.3%; m.p. 220-240°C.

Preparation of Block Copolymers

1. Copolymers of Depolymerized Cellulose Triacetate (CTA) and Diisocyanates.

Depolymerized cellulose triacetate (0.002 mole) was dissolved in a mixture of methylene chloride (50 ml) and ethylene chloride (25 ml) contained in a 250-ml 2-necked flask fitted with an agitator and a condenser. The flask and

TABLE I

Summary of Copolymer Properties

	Original			Deacetylated	
Copolymer	Yield %	[η] *	Softening Range (°C)	[η] **	Acetyl Value†
CTA-MDI	70	0.37	180-240	0.35	9.0
CTA-TDI	90	0.41	245-260	0.36	9.8
PPG-MDI-CTA	85	0.33	300-310	0.43	10.3
PPG-TDI-CTA	89	0.64	315-330	0.52	10.7
CTA (depolymerized)	93	0.16	210-222‡		10.6

*In CH_2Cl_2/CH_3OH (9/1) solution @ 25°C.

**In DMSO solution @ 30°C.

†Average of two determinations. Acetyl value of 10% corresponds to a D.S. = 0.42. The modified Eberstadt procedure (6) was used to determine the acetyl values.

‡Melting range.

contents were heated with agitation and azeotropically distilled to dry the system. About 25 ml of distillate was collected. Then either diphenylmethane diisocyanate (MDI) or m-toylene diisocyanate (TDI) (0.002 mole) was added under nitrogen. After solution was complete, triethylamine (0.15 ml) was added and the mixture agitated for 7 hr at 70°C. Ethylene chloride (50 ml) was added and the agitation continued overnight at room temperature. The reaction mixture was filtered through a coarse sintered glass filter, the solvent evaporated under reduced pressure to near dryness, the solid washed with ethanol and then soaked in a 2:1 ethanol:acetone mixture for 2 days. The resulting product was collected and dried at 60°C under high vacuum. Yield: 70% for the CTA-MDI, and 90% for the CTA-TDI copolymer.

2. Terpolymers of Cellulose Triacetate, Diisocyanates, and PPG.

A slightly modified procedure of Steinmann (4) was used. In a 250-ml 2-necked flask fitted with an agitator and Dean-Stark trap, with condenser and drying tube attached, depolymerized cellulose triacetate (0.002 mole) was dissolved in a mixture of methylene chloride (50 ml) and ethylene chloride (25 ml). The mixture was azeotropically distilled to collect 25 ml of distillate.

Into a 250-ml 3-necked flask equipped with an agitator, thermometer, N_2 inlet, and a Dean-Stark trap with condenser and drying tube attached, were charged polypropylene glycol (PPG) (1007 av. mol. wt; 0.002 mole) and ethylene chloride (7 ml). The mixture was azeotropically distilled and 4 ml of distillate collected. MDI or TDI (0.003 mole) was added to the PPG solution and the reaction mixture heated with agitation at 105°C for 3 hr and then the dry depolymerized cellulose triacetate solution was added. After a few min-

TABLE II

Enzymatic Degradation Results

	% Decrease in [η]						
Polymer	2 hr	5 hr	9 hr	10 hr	24 hr	48 hr	72 hr
CTA-MDI	6.1	31.4	-	54.3	61.4	71.4	-
CTA-TDI	14.7	20.8	-	36.1	55.6	69.4	-
CTA-MDI-PPG	25.6	33.0	-	40.0	68.6	74.4	-
CTA-TDI-PPG	14.9	21.4	-	26.2	49.9	62.1	65.0
Cellulose			15.4				

utes of agitation, triethylamine (0.15 ml) was added and the reaction mixture was agitated at 70°C for 45 hr. The resulting almost clear, viscous dope was diluted with ethylene chloride (50 ml), filtered through a coarse sintered-glass filter, and most of the solvent removed under reduced pressure. On washing the solid with ethanol, a colloidal solution formed. The polymer was separated by centrifuging; yields: CTA-MDI-PPG terpolymer, 85% (m.p. 300-310°C); CTA-TDI-PPG terpolymer, 89% (m.p. 310-315°C).

Deacetylation of the Block Copolymers

A modification of Vink's (5) procedure was used. Sodium (1.2 gm) was added to anhydrous methanol (300 ml) contained in a 3-necked flask equipped with an agitator and nitrogen inlet and outlet tubes. After solution was complete, the copolymer (10 gm) was introduced. The heterogeneous mixture was stirred continuously at room temperature for 3 hr.

In the case of the CTA-MDI and CTA-TDI copolymers, the solid was collected, washed with methanol, methanol-acetic acid (95:5), and methanol. In the case of the terpolymers, the reaction mixture was neutralized with acetic acid and the product recovered by centrifuging. It was washed with methanol three times. Each time separation was accomplished by centrifuging.

All the products were dried at 60°C under high vacuum. The intrinsic viscosity and acetyl values for the copolymers are summarized in Table I.

Enzymatic Hydrolysis

Cellulysin from Calbiochem Co. was employed. A 0.1% buffered (pH 5) enzyme solution was prepared using 0.05M Na acetate and HOAc. The copolymer (0.1 gm) was added to the enzyme solution (10 ml) contained in a screw-cap bottle and the bottle and contents incubated at 50°C for various times. The substrate was recovered by filtration, washed several times with

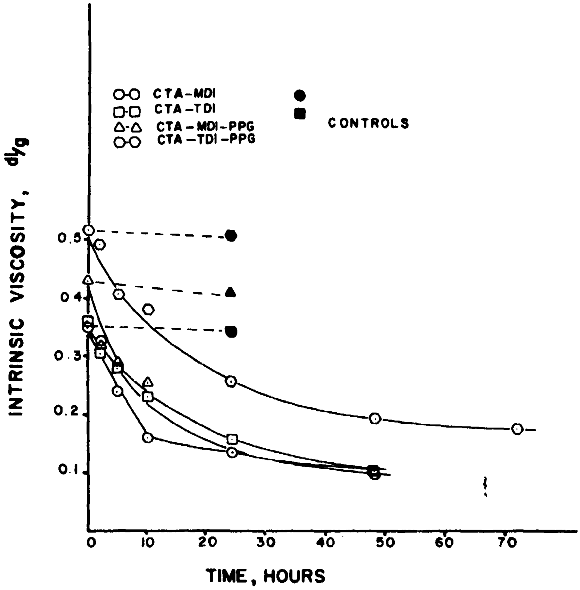

Fig. 1. Intrinsic viscosity vs. Time of Enzymatic Hydrolysis.

water, dried at 60°C under high vacuum, and its intrinsic viscosity determined. A control sample was run, in each case, in the absence of enzyme. Cellulose (Fisher brand filter paper) was incubated for 9 hr and its intrinsic viscosity determined in Cuene solution.

Results and Discussion

Two block copolymers were prepared by reacting equimolar amounts of the CTA oligomer with either MDI or TDI. Two block terpolymers were prepared by capping PPG with either MDI or TDI and then reacting with the CTA oligomer. Each polymer was deacetylated and incubated with cellulysin at 50°C. The enzymatic hydrolysis was monitered by intrinsic viscosity measurements. The results are summarized in Table II and Figure 1. In each case, a control was run in the absence of the cellulysin. The acid hydrolysis of the polymers was negligible.

There was a substantial decrease in the intrinsic viscosity for each of the copolymers, even at 10 hr incubation time. Cellulose showed a somewhat smaller decrease after 9 hr. incubation time-15% vs 26-54% for the block polymers after 10 hr – but this is probably due to the lower accessibility of cellulose compared to the amorphous block copolymers.

It is apparent that the incorporation of cellulose oligomer blocks in a polymer will result in biodegradability. There appears to be a polymer composition effect as the copolymers containing MDI appear to degrade more rapidly initially than those containing TDI. It is gratifying that the block copolymers appear to degrade more rapidly than cellulose itself.

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Received August 13, 1973
Revised September 30, 1973

ON THE EFFECT OF IONIZING RADIATION ON HYDROCARBONS AND POLYETHYLENE IN THEIR CRYSTALLINE STATE

According to extensive past work (1,2,3), ionizing radiation produces three principal permanent chemical modifications in polyethylene or hydrocarbons in general: crosslinking, double bonds, and chain scission—events which are generally considered to occur randomly along the chains. In the particular case of cross-links, the assumption of a random crosslink distribution, when applied to the traditionally envisaged randomness of the polymer structure (statistical coil in the amorphous state, the fringed micelle model in the crystalline state), has led to the basic simplifying assumption that intramolecular cross-links occur only in negligible proportions and hence practically all cross-links are effective in forming networks. Or conversely, according to this assumption, a characteristic network property, such as the insoluble fraction (gel content) or modulus, should completely define the number of crosslinks. In fact, the crosslink content has always been assessed on the basis of this assumption in the past and all comparisons with theories have relied on such assessments.

The justification of this approach relating to crosslinks has been challenged by Salovey and Keller (4) and followed up by extensive subsequent supporting confirmatory work pursued by these authors and various co-workers independently (5-11). Most of this work relied on solubility studies (gel content). In brief, it was inferred that in a chain-folded system of polyethylene the cross-links occur preferentially in the fold region, yielding a large and variable proportion of crosslinks which are ineffective in network formation. The network forming effectiveness of the crosslinks could be increased by improved interlamellar contact, or conversely decreased by reducing this contact, and hence it was inferred that those crosslinks which tie the consecutive chain-folded layers together play a particularly significant part in network formation. These, to our mind, fundamental assertions, however, have left little impression on the field.

More recently the above enquiry has been renewed. We believe that in the course of it, definitive support has been obtained for the original postulates. In addition, the new results relate not only to crosslinking, but also to double-bond formation and scission embracing not only polyethylene but also non-polymeric hydrocarbons.

The new work relies on a combined application of selective oxidative degradation of chain-folded crystals of polyethylene and on the determination of the full molecular weight spectrum by gel permeation chromatography (12,13). It is known that oxidizing agents, such as nitric acid or ozone, selectively cut the folds. This gives rise to chain fragments consisting of single (one fold stem), double (two stems plus fold), and multiple chain traverses through the

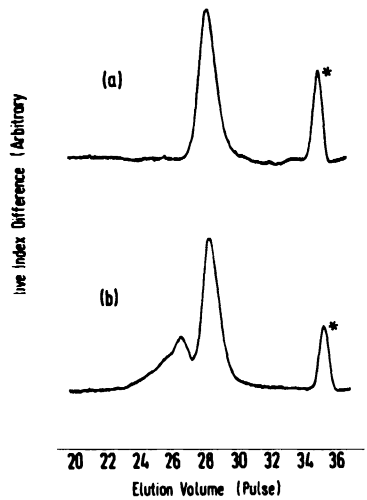

Fig. 1. Gel permeation chromatograms of a dicarboxylic acid obtained from monolayer crystals of chain-folded polyethylene by the removal of the fold surface through the degrading action of ozone. (a) Trace of the unirradiated dicarboxylic acid. The position of the principal peak corresponds to 95Å. (b) The same material as in (a) irradiated with γ rays to a dose of 600 Mrads. The smaller peak at the larger elution volume corresponds to the dimer molecule. Both in (a) and (b) the peaks marked with an asterisk are due to decane used as a calibration standard (20).

crystal, all with carboxylic end groups at the cut ends. These fragments manifest themselves as discrete peaks at the low molecular weight end of the GPC spectrum. When all the folds are cut the product consists of single traverses only, which are thus long-chain dicarboxylic acids of highly uniform chain length (14,15).

In addition to chain-folded polyethylene single crystals, we also used dicarboxylic acids obtained by the above degradation method for the radiation studies. By choosing different initial fold lengths (obtained by crystallizing and annealing polyethylene at different temperatures), we could obtain dicarboxylic acids of different lengths. These lengths are comparable to, but somewhat smaller than, the thickness of the original polyethylene crystal layer (allowing for chain inclination where this pertains) because the oxidizing agent not only cuts the folds but also shaves off the whole surface layer containing the folds.

All irradiations were carried out with ^{60}Co γ rays. The conclusions reached in this work relate to all three principal chemical effects produced by the radiation, namely crosslinking, double bonds, and scission. These conclusions, together with the broad outlines of the experiments by which they were arrived at, will be reported in this note. The analytical details will be given later.

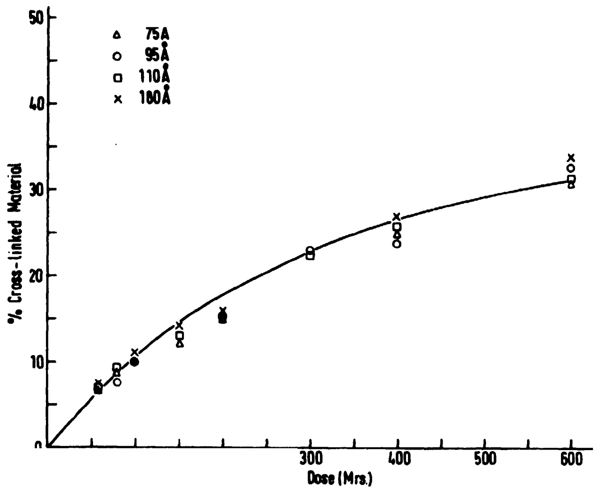

Fig. 2. Percentage of total crosslinked material formed from dicarboxylic acids of different lengths on γ irradiation with increasing dose. In the present context the emphasis is on the near coincidence of the points for the different materials at a given dose rather than on the dose dependence itself.

Crosslinking

Dicarboxylic acids were obtained as above in the form of monolayer crystals. These were irradiated with doses large enough that some insolubility (gel) would be expected from the existing literature data for hydrocarbons, on the assumption that a carboxylic end-group will not affect the crosslinking behavior of methylene groups in other than in their immediate vicinity.

It was found that contrary to expectations, all material remained fully soluble even up to 600 Mrads, the maximum dose, and further that the soluble product contained only a very small amount of cross-linked material, most of it corresponding only to the dimer stage with a slight amount of trimer. Figure 1 shows one example. It illustrates the effect of a dose of 600 Mrads on the molecular weight distribution of a dicarboxylic acid with a peak chain length of 96Å. From a G (crosslink) value of unity – an average figure based on the literature when allowing for the falling off of the G value with dose, 1.22 crosslinking points are expected per molecule which should give substantial amounts of gel and of course a large amount of high molecular weight material even in the soluble fraction. As can be seen, the experiment decisively refutes this expectation.

When dicarboxylic acids of different lengths were compared, it was found that the weight fraction of crosslinked material (identified by the fractional area of the chromatogram beyond that of the original single-molecule peak) was independent of the length of the original dicarboxylic acid. This is shown in Figure 2. It follows that the number of crosslinks produced by a given dose

per unit mass is not invariant (characterizable by a constant G value), but is inversely proportional to the length of the chain, which means that it is determined by the number of molecules present in a given amount of material. It was found further that the peak designated as dimer peak corresponded very closely to twice the molecular length of the unirradiated material, which in view of the fact that GPC measures hydrodynamic volume, means that the dimer chain must be very nearly twice as long in its extended form as the monomer in contrast to what would be expected if two chains were linked in random fashion along their full length. These points together conclusively prove that the chains are linked at or near their ends, and only in this way, from which it follows that there are no crosslinks between the parallel chains within the paraffinoid lattice. As if the carboxyl groups can have no direct influence beyond one or two chain members, this should be a characteristic property of paraffinoid lattices in general. (The exact chemical process of the end-linking was not followed up. As simultaneous reduction of carboxyl groups was also observed it is possible that it follows the removal of carboxyl groups. Decarboxylation is an established process in the radiation chemistry of fatty acids (2)).

A single scouting experiment was carried out on the paraffin n-$C_{36}H_{74}$ by irradiating it both in the crystalline state and in the molten form. As observed by Salovey et al. (16), a small second peak occurred, corresponding to the dimer range in both cases. However, we observed a small but noticeable difference in the positions of the minor peaks in the two cases, the peak for the melt-irradiated sample being at higher elution volume. The gross dimer compposition being taken for granted, this means that the latter samples should be more branched (smaller hydrodynamic volume!). This trend in itself is consistent with linking at chain ends in the crystal and random linking in the melt. The exact calibration showed that the cross-linked product in the sample irradiated while crystalline was indeed much closer to what was expected from end-linking. Without affecting the basic conclusion concerning linking in the chain-end region versus more random linking arising from this comparison, the agreement with end-linking was nevertheless not as close as in the case of the dicarboxylic acids, allowing for a small amount of branching in the dimer product even when irradiated in the crystalline state.

Polyethylene single crystals were irradiated up to 400 Mrads and subsequently degraded with ozone. The GPC traces of the irradiated samples were all very similar, and did not differ in essential respects from those given by the unirradiated samples. In particular, the usual peaked distribution sequence was obtained until only the single-traverse peak was left. As indicated in a previous preliminary publication (17), this should be proof in itself that there are no cross-links in the crystal interior, otherwise, e.g., the single traverse peak could never be obtained. Nevertheless, this conclusion is unconditionally true only if the cross-linking points are not cut within the crystal interior. If cross-links were present in the lattice and if in addition the chains were cut at the corresponding tertiary carbon atoms together with the folds, there would be

no multiple traverses left, but at the same time a low molecular weight spread would be added to the single traverse. As a small low molecular weight tail of the single traverse could indeed be observed for the highest irradiation doses, it appeared that the issue could not be completely settled without a detailed quantitative evaluation of this tail. Nevertheless, the need for such an analysis could be bypassed thanks to the following supporting facts obtained from the concurrent work on the hydrocarbons:

(a) We found that there are no crosslinks within the paraffinoid lattice. Applying this finding to polyethylene it would follow that such links within the fold stems need not be considered a fortiori.

(b) Degradation experiments on irradiated dicarboxylic acids have yielded a low molecular weight tail of closely similar magnitude to the corresponding polyethylene which in the case of the acids could be identified with scission at the newly created double bonds. It is evident that this also accounts for the tail in the case of polyethylene. This loophole having been closed, it can be asserted that in chain-folded crystals the crosslinks must be confined to the fold surface which is shaved off by the oxidizing agent.

This above conclusion of course was the inference from the original solubility experiments (4-11) now directly confirmed by the new, more specific evidence. In fact, the preference for the crosslinks to be at the fold surface turned out to be much more definitive than could have been anticipated from the previous work. The inferences, that parts of the crosslinks would be ineffective for network formation by creating rings within the loops of the folds and that the network-forming links would be those linking adjacent fold planes within the same layer and folds between superposed layers, remain valid, indeed greatly strengthened. The last type of linking would be affected by sedimentation conditions in the case of solution grown crystals and by crystallization conditions in the bulk as indeed is observed (3,11,18).

Double Bonds

Irradiated dicarboxylic acid samples of different lengths were examined for trans-vinylene double bond content by infrared spectroscopy. It was found that the double bond concentration was totally independent of chain length and thus independent of the number of molecules present. This leads to the conclusion that in contrast to crosslinks, the formation of double bonds is equally probable everywhere along the chain, hence its distribution must be random.

In undegraded chain-folded polyethylene crystals, however, the number of double bonds relative to the number of methylene groups was lower than in the corresponding dicarboxylic acid. It follows that the density of double bonds in the fold region (which has been shaved off to yield the dicarboxylic acid) must be lower than in the paraffinoid lattice. This nonuniformity of the double bond distribution over the crystal is contrary to accepted ideas on double bond formation. We may tentatively attribute it to enhanced vinylene decay in the fold surface region which could readily follow from the fact that the crosslinks form in that region as just established.

Chain Scission

Some salient observations were made also as regards chain scission. No chain scission could be inferred from the GPC traces of the dicarboxylic acid crystals as a result of irradiation. The absence of any additional material at the low molecular weight tail is apparent even by inspection of Fig. 1. By quantitative assessment of our results, this means that if chain scission is present at all this must involve less than 0.05 cuts per unlinked molecules in the case of Figure 1. Thus the chains are not being cut within the paraffinoid lattice.

The above conclusion, when applied to chain-folded polyethylene, would mean that scission, generally claimed to occur, ought to be confined to the fold surface. Nevertheless, by our recent experiments on single crystals of polyethylene, 100% insolubility could be reached at a dose of 600 Mrads. The existence of a residual soluble fraction has been usually taken as the evidence for a scission reaction in polyethylene. We see that by our data there is in fact no justification for involving chain scission in the radiation chemistry of polyethylene. If any were present in such small amounts, as would be detectable only by mass spectrometry, this is of no consequence for the solubility behavior, and hence does not concern us in the present work. It is to be added that in the polyethylene used here (Marlex 6009), all material below a molecular weight of about 6000 was removed by fractional crystallization prior to the present study. Noticeable residual solubilities in earlier studies from our laboratory (8,9) are attributable to the presence of such low molecular weight material. Of course, its presence has been allowed for when evaluating solubility data in terms of simultaneous scission and crosslinking reactions (3). However, it needs bearing in mind that such low molecular weight material is not likely to be randomly distributed, as is generally assumed, but can be largely segregated during crystallization. For this reason the effect of the low molecular weight material on the solubility could be greater than usually envisaged. It needs adding that the existence of chain scission has been questioned before by Rijke and Mandelkern, who could obtain 100% gel by using well defined fractions (3,19).

Summing up, our main conclusions are as follows:

(1) There are no cross-links within the paraffinoid lattice up to doses of 600 Mrads (the highest used here). In nonpolymeric hydrocarbon crystals, the crosslinks, such as there are, link chains at their ends, and in chain folded polyethylene they are situated exclusively within the fold surface and may form links either in the fold region of the same molecule or between folds of other molecules.

(2) Transvinylene double bonds are uniformly distributed within the crystalline lattice, but there is a reduced concentration of such double bonds within the fold region of polyethylene.

(3) There is no chain scission within the paraffinoid lattice (within the

accuracy of 0.05 cuts per chain traverse of 95Å) and by existing results there is no reason for invoking chain scission, even in the composite amorphous-crystalline system of chain-folded polyethylene.

We are greatly indebted to Professor A. Charlesby and Dr. P. Fydelor, Royal Military College, Shrivenham for the irradiation of our samples and for numerous constructive discussions. One of us, G. N. Patel, wishes to thank the Science Research Council for financial support.

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Received August 2, 1973

COMPLEX FORMATION OF METHYL METHACRYLATE WITH ZIEGLER-NATTA CATALYST COMPLEX IN CARBON TETRACHLORIDE MEDIUM*

Introduction

Stereospecific polymerization of methyl methacrylate with Ziegler-Natta catalyst systems such as $VOCl_3$-$AlEt_3$ (1) and VCl_4-$AlEt_3$ (2) in hydrocarbon media was earlier studied in our laboratory. Some work on polymerization of methyl methacrylate in polar solvent, such as acetonitrile (3) was also reported. C. Eden and H. Feilchenfeld observed that transition metals and their salts in lower valency state can be oxidized to higher valency state in presence of carbon tetrachloride. They found that carbon tetrachloride had an inhibiting effect on reduction of transition metal halides by aluminium alkyls. Ziegler-Natta catalyst systems have been mostly employed in nonpolar medium for polymerization reactions and Ziegler in his patent gave a long list of solvents for polymerization of α-olefins (K. Ziegler, Israel Pat. 8390), but carbon tetrachloride was not among them. Therefore it is interesting to study polymerization of methyl methacrylate with Ziegler-Natta catalyst system in carbon tetrachloride medium.

The polymerization of methyl methacrylate with stereospecific catalyst systems such as $TiCl_4$-$AlEt_2Br$, VCl_4-$AlEt_2Br$, and $VOCl_3$-AlE_2Br has not been studied in carbon tetrachloride medium. In this present investigation we observed that these catalyst systems in carbon tetrachloride medium yield stable Ziegler-Natta catalyst complexes (ZC) which can be isolated. Further, it was observed that these catalyst complexes (ZC), when aged for 24 hours and allowed to react with methyl methacrylate, gave new complexes (MC).

Experimental

Transition metal halide solution of (1) $TiCl_4$, (2) VCl_4, and (3) $VOCl_3$ in hexane were added to three 50-cc Erleyenmeyer flasks containing carbon tetrachloride. To these homogeneous solutions, solution of aluminium diethyl bromide in hexane was added at a molar ratio of aluminium to transition metal equal to 4. Instantaneously a black precipitate was formed in all the three cases. After an induction period (5), decomposition took place with evolution of gases, and a large amount of heat was produced. The heterogenous solutions of catalyst components were well stirred and aged for 24 hr in order to keep transition metal halide in the highest valency state (4). A specific amount of methyl methacrylate was added in all of the three different flasks and the reac-

*NCL Communication No. 1762.

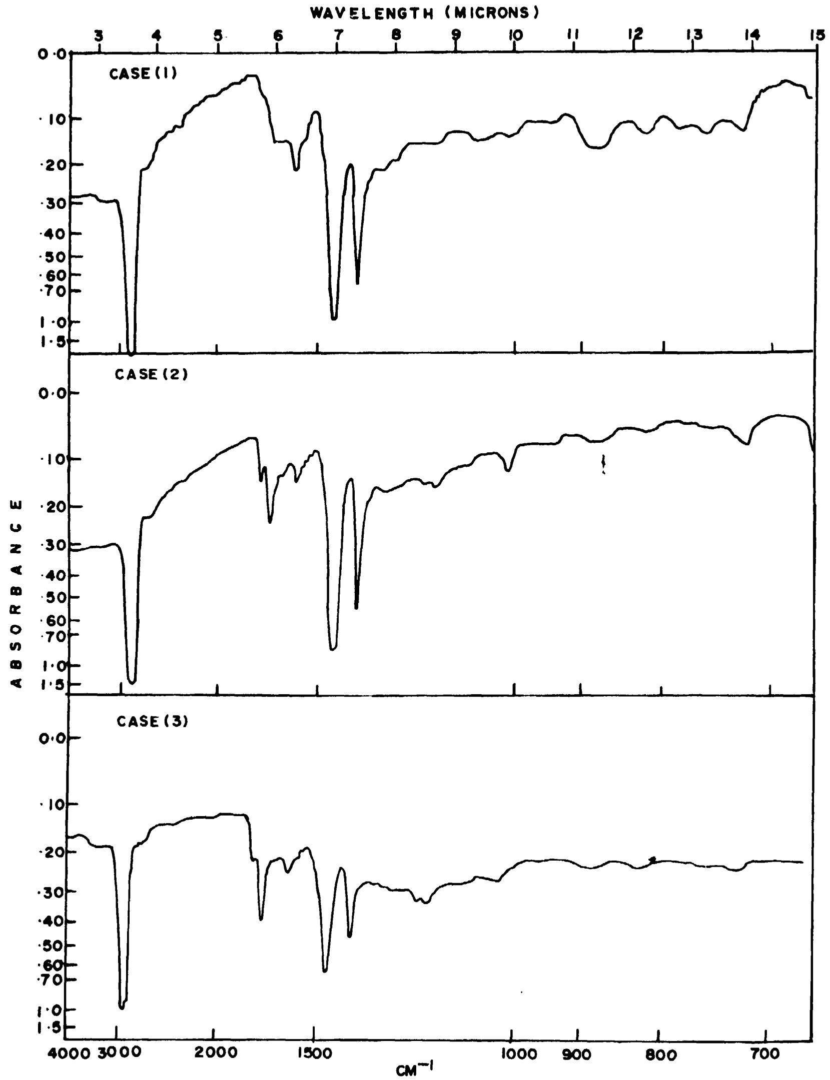

Fig. 1. IR spectra of complexes (MC) of methyl methacrylate after reaction with Ziegler-Natta catalyst system: case (1) $TiCl_4$-$AlEt_2Br$; case (2) VCl_4-$AlEt_2Br$; case (3) $VOCl_3$-$AlEt_2Br$.

tion systems were allowed to polymerize in close conditions for three hr at 40°C. The reactants were added inside a dry box under the purging of pure nitrogen gas. When reactants were poured in a large amount of methanol containing 10% hydrochloric acid, brown complexes (MC) were separated in cases (2) and (3), while the black precipitate was separated in case (1). The products were purified by dissolving in chloroform and reprecipitation in methanol.

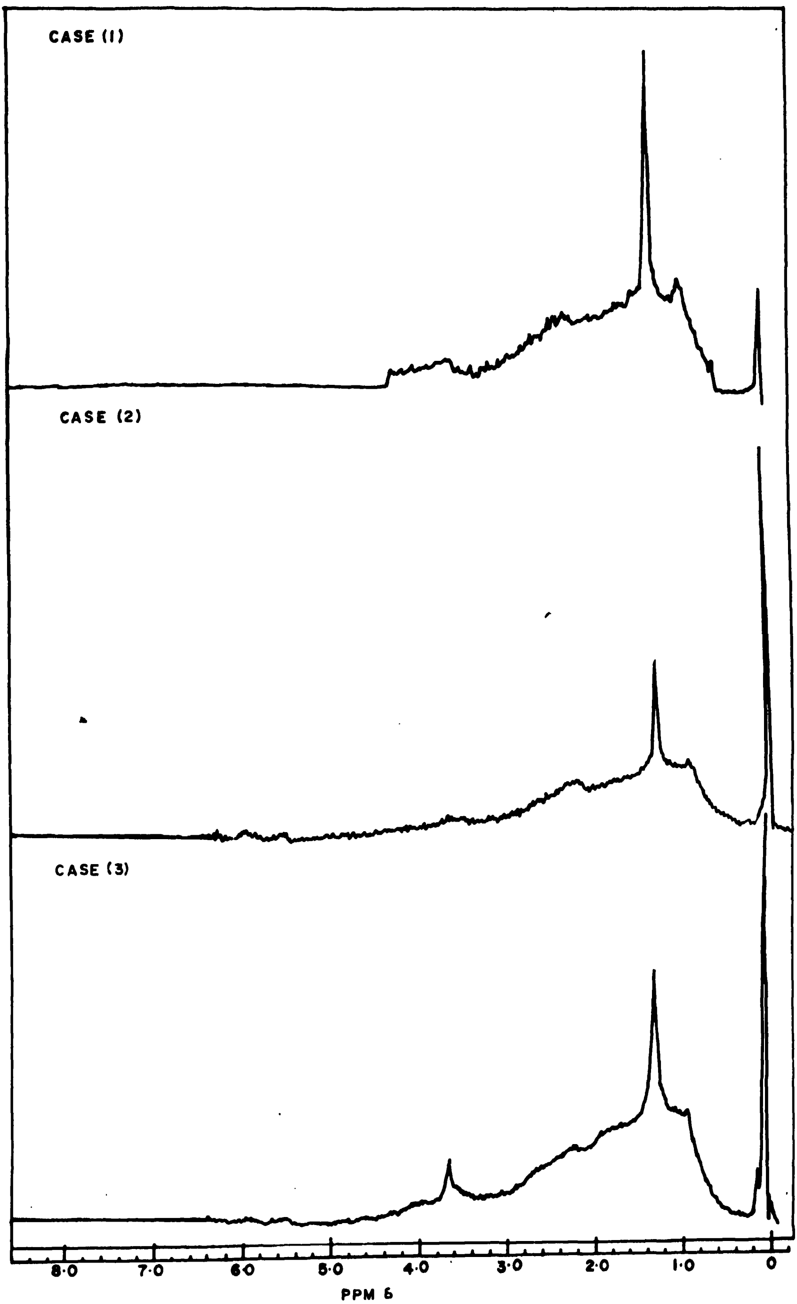

Fig. 2. NMR spectra of complexes (MC) of methyl methacrylate after reaction with Ziegler-Natta catalyst systems: case (1) $TiCl_4$-$AlEt_2Br$; case (2) VCl_4-$AlEt_2Br$; case (3) $VOCl_3$-$AlEt_2Br$.

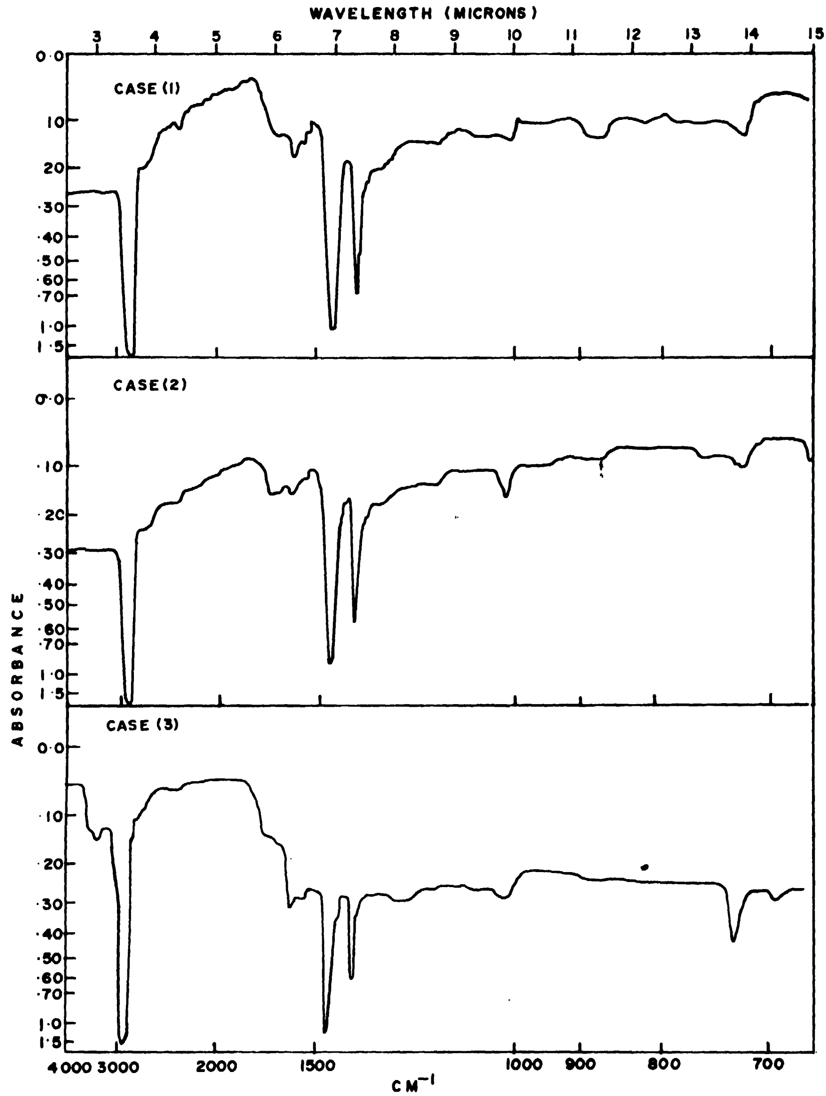

Fig. 3. IR spectra of Ziegler-Natta catalyst complexes (ZC): case (1) $TiCl_4$-$AlEt_2Br$; case (2) VCl_4-$AlEt_2Br$; case (3) $VOCl_3$-$AlEt_2Br$.

The purified dark brown complexes were highly crystalline and stable up to 350°C.

IR spectra of all purified samples in nujol were recorded with Perkin Elmer Infracord 137B spectrophotometer. NMR spectra of purified samples in chloroform were recorded on a Varian A-60 M cps spectrophotometer at room temperature by using 3% (wt/vol) solution.

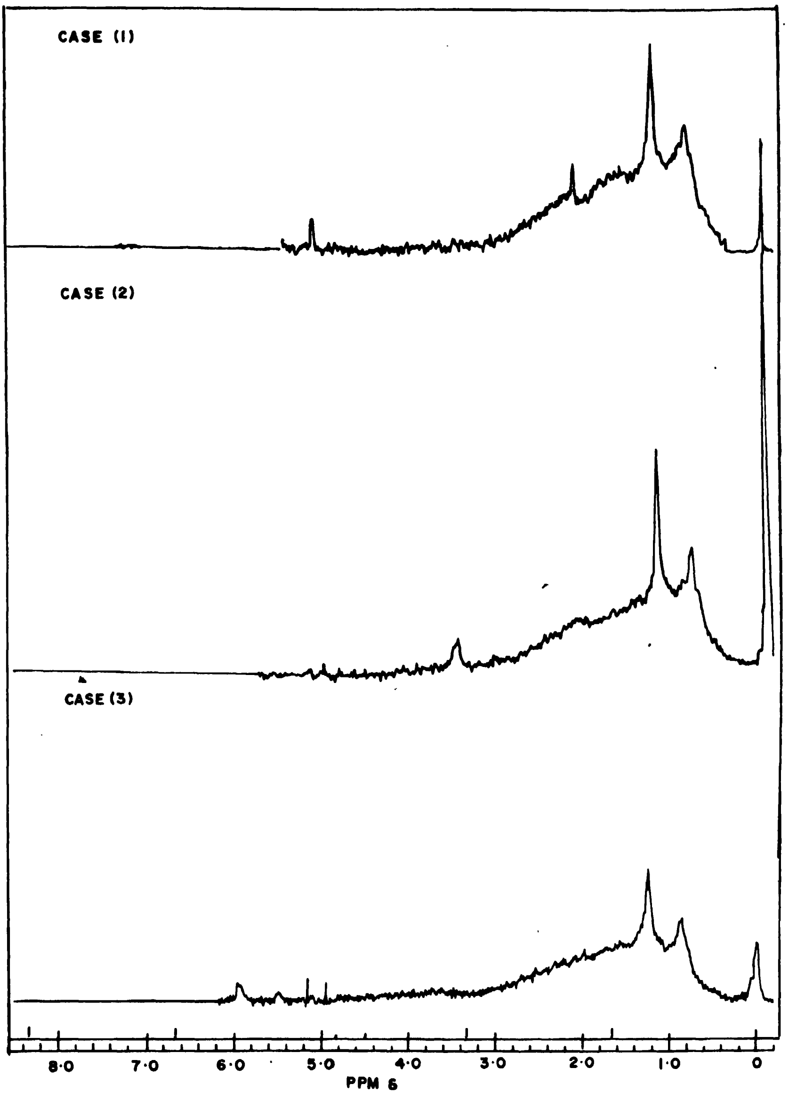

Fig. 4. NMR spectra of Ziegler-Natta catalyst complexes (ZC): case (1) $TiCl_4$-$AlEt_2Br$; case (2) VCl_4-$AlEt_2Br$; case (3) $VOCl_3$-$AlEt_2Br$.

Results and Discussion

IR spectra of the samples (Fig. 1) in cases (2) and (3) showed a predominant absorption peak at 1700 cm^{-1} due to the C=O group of methyl methacrylate while this type of absorption peak was not seen in IR spectra of the sample in case (1). Figure 1 also shows the absence of absorption peaks at 1160 cm^{-1}, 1200 cm^{-1}, 1300 cm^{-1} due to $-OCH_3$ group of methyl methacrylate in

TABLE I

Elemental Analysis of Complexes

	'C'	'H'	'Cl'
A. Complexes (MC) of methyl methacrylate after reaction with Ziegler-Natta catalyst systems			
1. $TiCl_4$-$AlEt_2Br$-CCl_4-methylmethacrylate	79.6	7.41	7.06
2. VCl_4-$AlEt_2Br$-CCl_4-methylmethacrylate	80.24	7.25	6.04
3. $VOCl_3$-$AlEt_2Br$-CCl_4-methylmethacrylate	84.55	8.91	6.83
B. Ziegler-Natta catalyst complexes (ZC)			
1. $TiCl_4$-$AlEt_2Br$-CCl_4	81.43	9.08	7.59
2. VCl_4-$AlEt_2Br$-CCl_4	70.84	7.77	13.06
3. $VOCl_3$-$AlEt_2Br$-CCl_4	80.41	7.60	5.03

all the three spectra. The absence of $-OCH_3$ group in each IR spectra was confirmed by NMR spectra (Fig. 2) of all these samples. From these observations it can be concluded that in cases (2) and (3) methyl methacrylate had reacted with Ziegler-Natta catalyst complex (ZC) to form a new complex (MC) and while reacting with these complexes (ZC) the $-OCH_3$ group of methyl methacrylate must have been knocked off. There was no such reaction between Ziegler-Natta catalyst complex (ZC) and methyl methacrylate in case (1).

Further, it was observed that when only the catalyst mixture was poured in acidified methanol after 24 hr aging and three hours reaction time at 40°C, a black precipitate (ZC) separated out in all three cases. The IR (Fig. 3) and NMR (Fig. 4) spectra of these three samples (ZC) are identical showing the presence of C–Cl only. This observation leads one to conclude that the formation of Ziegler-Natta catalyst complex (ZC) in carbon tetrachloride medium has taken place.

Elemental analyses of these Ziegler-Natta catalyst complexes (ZC) alone and their products after reaction with methyl methacrylate (MC) is shown in Table I. This analysis also supports the formation of complexes (MC) of methyl methacrylate with Ziegler-Natta catalyst complex (ZC) in cases (2) and (3) but not in case (1). TGA, DTA, BM, UV, and mass spectra analyses of these complexes will throw more light on the structure of these complexes.

In order to know the mechanism of these reactions between Ziegler-Natta catalyst complexes (ZC) and methyl methacrylate, kinetic studies with these catalyst systems are being carried out.

Work on polymerization of isoprene with these catalyst systems is also in progress.

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POLYMER LETTERS EDITION VOL. 11, PP. 753–754 (1973)

PREPARATION OF THE SKINNED MEMBRANES WITHOUT EVAPORATION STEP

Introduction

Manjikian type cellulose acetate membranes are prepared by using a casting solution of Eastman CA-39.8-3 in a mixture of acetone-formamide (weight ratio of 25:45:30 respectively). This solution is then spread on a glass plate and exposed to the air for 30 sec and then submerged under water where the solvents are leached out and the membrane is formed (1).

Ever since the discovery of the skinned membranes by Loeb and Sourirajan (2), there has been a great deal of effort in order to understand the mechanism of their formation. There are, in general, two schools of speculation each with its experimental support: (a) one which believes the skin is formed because of the evaporation step involved (3-8), and (b) the one that suggests that the responsible cause is the precipitation (8-11).

This work reports the formation of skinned membranes even in the absence of an evaporation step, thereby suggesting that there is essentially a common mechanism involved in the formation of the membranes with or without evaporation.

Experimental Results and Discussion

In an attempt to obtain membranes without any evaporation a number of 10 mil thick films were prepared from a Manjikian casting solution (one at a time) inside a closed chamber saturated with vapors of both solvent components (by placing large trays of acetone and formamide as well as a container of dehydrated $CaCl_2$ for a day). Membranes obtained were glossy on the exposed surface, dull on the glass side, and were bulged upward, a clear indication of anisotropy.

Desalination performance of these membranes are demonstrated in Table I where they are compared with a Manjikian type membrane prepared from the same casting solution. These tests were done in a recirculating system with three identical thin channelled stainless steel cells as described elsewhere (12). The feed solution was 5000 ppm NaCl at 1500 psig.

This experiment then reveals that evaporation is not the only way of obtaining anisotropic membranes. In fact its elimination results in a thinner and denser skin which exhibits a higher flux and a higher rejection. In other words it suggests that there might be a common process involved in both methods which needs further elucidation.

TABLE I

Comparison Between Membranes with and without Evaporation

	No Evaporation		30 sec Evaporation	
	Unheated	Heated at 87° C (4 min)	Unheated	Heated at 87° C (4 min)
Flux(gfd)	74	13.9	128	13.2
Rejection %	30-40	97-99	10-24	97-98.5

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POLYMER LETTERS EDITION VOL. 11, PP. 755–757 (1973)

ELECTROCHEMICAL POLYMERIZATION OF TRIOXANE WITH TETRAETHYLAMMONIUM HEXACHLOROANTIMONATE

We have previously reported that the electrolysis of trioxane in nitrobenzene and ethylene dichloride by use of a silver or tetrabutylammonium perchlorate as electrolyte resulted in the formation of polyoxymethylene (1,2). The experimental results suggest that polymers form by the cationic mechanism. Asahara et al. reported the electrolytic polymerization of trioxane in dry tetrahydrofuran (3). So far only perchlorate or tetrafluoroborate salt has been employed in the electro-initiated cationic polymerization (4,5). Here we have used a new electrolyte, tetraethylammonium hexachloroantimonate, that has not yet received attention in the electrochemical polymerization although hexachloroantimonate, $(SbCl_6)^-$, derivatives of triphenylmethyl, and cycloheptatrienyl cations have been studied extensively as initiators for cationic polymerization (6-9).

The tetraethylammonium hexachloroantimonate was prepared and purified as described in the literature (10). It dissolves in nitrobenzene, tetrahydrofuran, and other organic solvents, and furnishes a good electrical conducting medium. The experimental procedures for polymerization were the same as in the previous paper (1).

When a trioxane solution (1.85 M) of nitrobenzene at 25°C with $(C_2H_5)_4N^+$ $SbCl_6^-$ was subjected to electrolysis at a fixed current, polymers formed exclusively in the anode compartment. No polymerization occurs if the solution is not electrolyzed. The data on polymerization initiated at several currents are summarized in Table I which demonstrates that polymer yields increase with

TABLE I

Electrochemical Polymerization of Trioxane (1.85) in Nitrobenzene Containing 1% Tetraethylammonium Hexachloroantimonate at 25°C

Current (ma)	Time of electrolysis (min)	Conversion (%)	η_{sp}/c (0.5g/dl)
4	60	64	1.21
6	60	72	1.15
8	50	70	1.08
10	40	65	0.96
15	35	70	0.68

TABLE II

The Polymer Formation with Different Initial Trioxane Concentrations at 6 mA and 25°C

Monomer conc. (M)	0.864	2.70	3.70
Polymer yield (g/hr)	0.490	1.60	2.17
η_{sp}/c (0.5 g/dl)	0.550	1.22	1.32

increase in current densities, whereas molecular weights of resulting polymers decrease. It is likely that the increase in current increases the concentration of the initiating species which, in turn, enhances polymerization rates and decreases polymer molecular weights. The polymer yields and molecular weights increase with monomer concentrations polymerized at a constant current of 6 mA (Table II).

The exploratory experiments showed that on electrolysis styrene, acrolein and tetrahydrofuran also polymerized with $(C_2H_5)_4N^+$ $SbCl_6^-$. The polymerization may have been initiated by the direct oxidation of trioxane at the anode and/or by the species formed by the electrolytic oxidation of hexachloroantimonate anions.

The authors wish to thank Ranchi University for giving the University Grants Commission of India Research Fellowship to one of us (A.G.).

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Received April 17, 1973
Revised September 10, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 759–765 (1973)

THE INVOLVEMENT OF SINGLET OXYGEN ($^1\Delta_g$) IN THE PHOTODEGRADATION OF POLYPROPYLENE. SPECULATION ON THE ORIGIN OF $^1O_2$ IN THE POLYMER

Singlet oxygen ($^1\Delta_g$, $^1O_2$) has been reported to attack C–C unsaturation in rubbers to give hydroperoxides (1), and to attack either unsaturated or saturated sites in polyethylene to give hydroperoxides (2). We have recently shown that many of the effective Ni(II) chelates commonly claimed to photostabilize polypropylene are extremely efficient quenchers of $^1O_2$ (3,4). Similarly, $^1O_2$ quenching has been demonstrated for various aromatic diamines used to stabilize rubbers (5). Taken together, these discoveries automatically lead to the suggestion that $^1O_2$ might well be an important factor in the photodegradation of polypropylene. This same suggestion was first made five years ago by Trozzolo and Winslow (6), but this possibility has not been fully explored.

The suggested involvement of $^1O_2$ leads to two pertinent questions:
a. Can $^1O_2$ contribute to the photodegradation of polypropylene?
b. What are the potential sources of the $^1O_2$ in the polymer system?
In this paper we shall offer partial answers to both of these points.

$^1O_2$ Reaction with Polypropylene and Hydrocarbons

$^1O_2$ addition to olefins to give allylic hydroperoxides (1,7) is well established, but Kaplan and Kelleher (2) have also reported a slow attack on fully saturated alkanes. To check the relative ease of attack at these two sites, liquid hydrocarbons were employed. Hexadecane was carefully purified by a combination of distillation and treatment with concentrated sulfuric acid to minimize unsaturated impurities. For solid-gas and solid-liquid reactions, $^1O_2$ can be conveniently generated by a microwave discharge with the apparatus that we have used previously (3). The purified undiluted hexadecane (3.4 M) gave no detectable hydroperoxides ($< 5 \times 10^{-6}$M) after 5.0 hr exposure to $^1O_2$ from the microwave source, and suggests that $^1O_2$ attack at saturated centers is unimportant under our experimental conditions. The hydroperoxide concentration was monitored by an iodometric method (8).

Since squalene (2,6,10,15,19,23-hexamethyltetracosane-2,6,10,14,18,22-hexaene) is a liquid model for the C–C unsaturation in polypropylene, squalene solutions (1.5×10^{-3}M) in hexadecane were also exposed to the $^1O_2$ stream. This resulted in 2.6×10^{-3}M hydroperoxide in 5.0 hr. In the presence of 3×10^{-3}M of nickel 2,2′thiobis (4-t-octylphenol) n-butylamine (a good $^1O_2$ quencher (3)) this same solution gave only 1.6×10^{-3}M of hydroperoxide in a 5 hr treatment.

The microwave discharge can produce $^1\Sigma_g$ $^1O_2$, atomic oxygen and ozone

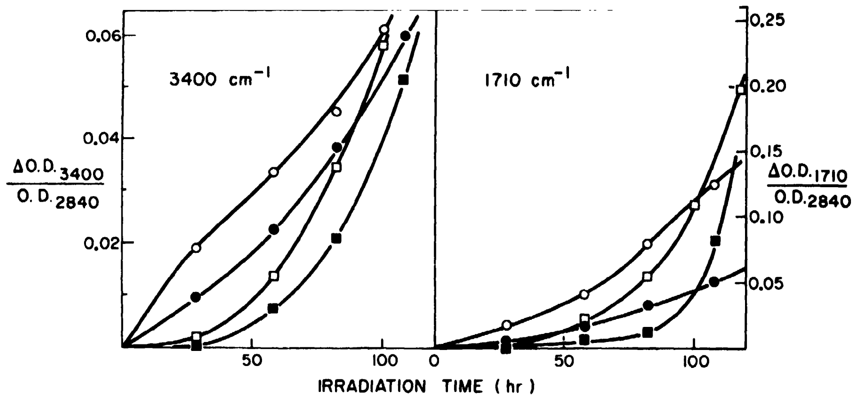

Fig. 1. Effects of $^1O_2$ pretreatments on the photodegradation of polypropylene films. ΔO.D./O.D.$_{2840}$ is the normalized optical density, corrected for variations in the analyzed sample thickness (see reference (11)). Transmission IR values: ■ is commercial polypropylene film; ● is film pretreated with $^1O_2$. ATR IR values (Ge element, 45° incidence): □ commercial polypropylene film; ○ film pretreated with $^1O_2$.

as well as $^1\Delta_g$ $^1O_2$; the $^1\Sigma_g$ $^1O_2$ and O_3 are normally assumed to be removed by the trap system (9). Atomic oxygen and O_3 will lead to carbonyl species as well as peroxide oxidation products. However, the possibility of atomic oxygen or O_3 contributing to the oxidation of the squalene was disproven by an IR analysis of the undiluted squalene exposed to $^1O_2$ until the peroxide concentration was ~1.0 M. The $^1O_2$ exposed squalene showed no detectable absorption in the carbonyl region (1750–1680 cm^{-1}) indicating a carbonyl concentration of less than 1 X 10^{-4}M. Hence there is no significant concentration of O or O_3 downstream from the cold traps in the microwave discharge system.

Commercial isotactic polypropylene films (Enjay cast, 22μ acetone Soxhlet extracted to remove additives) were exposed to the $^1O_2$ stream from the microwave discharge. The hydroperoxide concentration build-up in the film was found to be 5.0 X 10^{-4}M after 51 hr exposure, an unexposed film being peroxide free (< 1 X 10^{-5}M). From the squalene and hexadecane results with $^1O_2$, it is reasonable to conclude that the formation of polypropylene hydroperoxides results solely from $^1O_2$ attack on $>$C=C$<$, i.e., at the unsaturation present in most polypropylene chains (~0.05 M from the film IR absorption at 1645 cm^{-1}). This conclusion is consistent with the known ability of $^1O_2$ to diffuse significant distances (> 100Å) through hydrocarbon films before appreciable deactivation occurs (10), although the solid polymer-gaseous $^1O_2$ reaction is much slower than the stirred squalene solution-$^1O_2$ reaction.

In order to demonstrate the effects of $^1O_2$ pretreatment on the subsequent photostability of the polypropylene film, the 51 hr $^1O_2$ treated films and untreated films were irradiated in a Xenon arc Weather-Ometer (6000 watt at

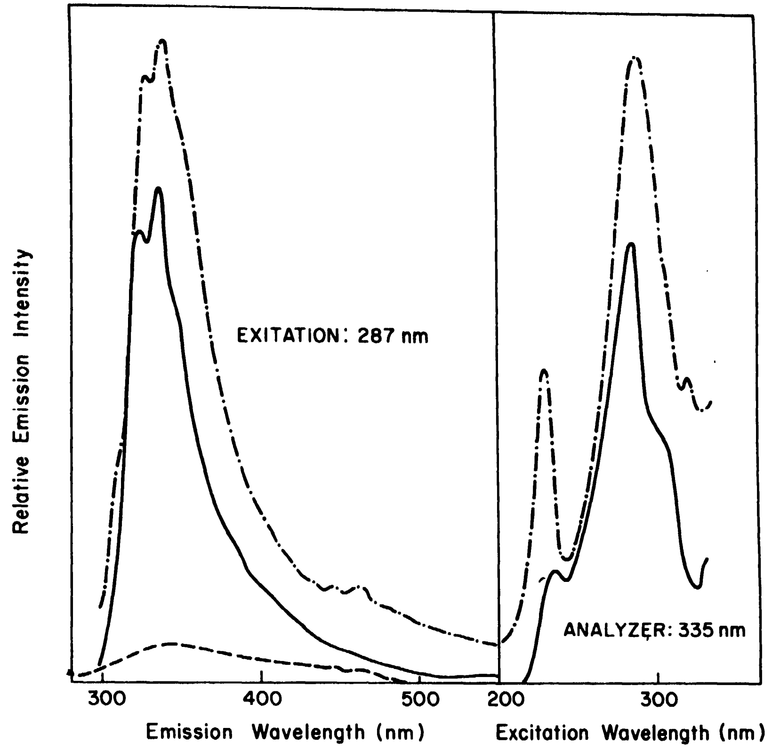

Fig. 2. Fluorescence emission from polypropylene films. ——— is film immediately after hexane extraction; —•—•— is untreated film and extracted film after ~10 days in urban air; and —— is naphthalene dissolved in 2,2,4-trimethylpentane. Uncorrected spectra: Xe source, IP28 photomultiplier tube, Farrand spectrofluorometer.

33°C) and the –OH (at 3400 cm^{-1}) and carbonyl (at ~1720 cm^{-1}) product build-up monitored periodically by transmission and attenuated total reflection IR (11). From these oxidation curves shown in Figure 1, it is obvious that $^1O_2$ treatment prior to UV irradiation has completely eliminated the usual induction period (~40 hr) and greatly accelerated the destruction of the film. (Untreated film normally fails on flexing after ~90 hr UV exposure). The product build-up curves also indicate that photo-oxidation is most rapid in the film surfaces for both film samples, since the surfaces concentration of each product (shown by the ATR curves) is appreciably greater than the average concentration (shown by the transmission curves) (11).

The Possible Origin of $^1O_2$ in Polyolefins

The stationary concentration of $^1O_2$ in the atmosphere is likely to be trivial in comparison with, for example, O_3 concentrations, so that atmospheric $^1O_2$

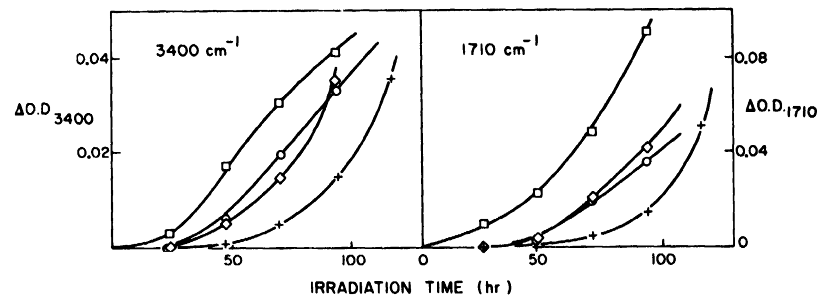

Fig. 3. Effects of aromatic additives on the photodegradation of polypropylene films. Transmission IR spectra: ○ is polypropylene alone; □ is polypropylene plus anthracene (0.004 M); + is polypropylene plus anthracene (0.004 M) + nickel dibutyldithiocarbamate (0.002 M); and ◇ is polypropylene plus phenanthrene (0.032 M).

can probably be ignored. Trozzolo and Winslow originally suggested that $^1O_2$ was generated in polyethylene by the quenching of UV-excited macroketonic impurities in the polymer by ground state oxygen (6). Although this is a viable process, the large concentrations of polynuclear aromatics (PNA) released into the atmosphere from combustion processes (e.g., 0.02 g/car/hr) (12), and the demonstrated ability of PNA impurities to concentrate in polyolefin articles ecposed to this air (13,14,15) makes these compounds potential candidates for $^1O_2$ sources in polyolefins.

Luminescence emission from polyolefins has frequently been reported (13, 14,15) and although it was originally attributed to macro aldehydes or ketones, it is now believed to result from PNA impurities including naphthalene, anthracene, and phenanthrene (or their derivatives) at low concentrations (10^{-3} – 10^{-5} M) in equilibrium with atmospheric PNA contaminants (13,14,15). Commercial polypropylene films which we have examined all show the distinctive emission spectrum of a naphthalene at ~10^{-3} M (Fig. 2), the equilibrium concentration reported by other workers (15). Phenanthrene and anthracene (10^{-4} – 10^{-5} M) were also detected by their fluorescence in films exposed to city air for ~7 days. The emissions from these PNA compounds was less than for naphthalene, and overlap with the emission from the latter compound made quantitative estimation difficult. PNA impurities can be removed by hexane washing as can the naphthalene impurities shown in Figure 2, but build up again within ~10 days on storage in air.

Many PNA compounds can efficiently generate $^1O_2$ by reaction 1 (quantum yield for $^1O_2$ production of up to 0.8 (16)) when exposed to sunlight (>290 nm) due to PNA triplet (T*) quenching by ground state ($^3O_2$) oxygen (17).

$$S_0(PNA) \xrightarrow{h\nu} S_1(PNA) \longrightarrow T^*(PNA) \xrightarrow{^3O_2} S_0(PNA) + {}^1O_2 \ .. \qquad (1)$$

Furthermore some PNA compounds (anthracene, rubrene etc.) can themselves

combine with $^1O_2$ to give endoperoxides (7). Thus PNA impurities in (UV transparent) polyolefins may absorb sunlight, generate $^1O_2$, and also react to give photo-unstable peroxides (7).

The possibility that PNA impurities in polypropylene samples might act as in situ sources of $^1O_2$ which can then either diffuse away to attack allylic $-CH_2-$ groups, or give photosensitive endoperoxides, is supported by the effects of deliberately introduced PNA concentrations on the photostability of the Enjay polypropylene film. The additives were all introduced by immersing films in 2,2,4-trimethylpentane solutions of either anthracene, phenanthrene or naphthalene (0.08 M) or anthracene (0.08 M) + nickel dibutyldithiocarbamate (0.2 M). The transmission IR curves for –OH and carbonyl build-up (Fig. 3) both show that anthracene can markedly accelerate the photodegradation, despite the fact that both anthracene and phenanthrene sublimed out of the film completely during ~40 hr Xenon arc exposure (ambient temperature ~33°C). Napthalene (~10^{-3}M) was lost completely within ~10 hr, and not surprisingly showed no sensitization under these irradiation conditions (not shown).

The inclusion of the nickel dibutyldithiocarbamate stabilizer (a very efficient $^1O_2$ quencher (3)) prevented the anthracene sensitization, and even stabilized the film beyond the lifetime of the additive free film sample (Fig. 3). However, as well as $^1O_2$ quenching, this chelate might also quench anthracene triplets, as reported for several other Ni(II) chelates (18,19) and is also an efficient decomposer of polypropylene hydroperoxide (20).

The lack of sensitization by phenanthrene might result from several sources e.g. low efficiency of $^1O_2$ generation from the triplet (21), or low triplet concentration (phenanthrene has an order of magnitude lower extinction coefficients from 290–360 nm than has anthracene). Also phenanthrene does not react with $^1O_2$ to give an endoperoxide (7). Anthracene sensitization via radical precursors is a possible alternative process to $^1O_2$ generation, but can be ruled out since direct radical formation from the lowest excited singlet or triplet states of anthracene is unlikely due to the low energies of these states ($\leqslant$ 74 Kcal m^{-1}) (22). Radical generation by a biphotonic process has been detected in the e.s.r. spectra of UV-exposed phenanthrene containing polyethylenes (23), and naphthalene containing polypropylene (15), although anthracene was not found to undergo this reaction.

In further support of the possible importance of polynuclear aromatics in polyolefin photodegradation, it should be noted that Pivovarov and Lukovnikov (24) have reported that efficient organic UV stabilizers for polypropylene, such as 2-hydroxy-benzophenones and substituted triazoles, quench PNA emissions from polyolefins, possibly by long range energy transfer. Similarly various Ni(II) chelates which are also effective polypropylene UV stabilizers have been shown to quench PNA triplet states at close to diffusion controlled rates in solution (18,19). This quenching will, of course, minimize the formation of $^1O_2$ from the excited aromatics, and so suppress the subsequent formation of photo-vulnerable peroxides.

In conclusion, we have shown that $^1O_2$ can attack commercial polypropylene films to yield hydroperoxides, probably from backbone allylic-CH_2-sites, and that $^1O_2$ pretreatment drastically accelerates photodegradation of these films due to the presence of photo labile hydroperoxide groups (7). In addition, we have presented some evidence in support of the contention that certain PNA impurities might play an important role in reducing the photodegradation induction period by generating $^1O_2$ within the polymer, which can react with unsaturation to give hydroperoxides and possibly also by reacting themselves with $^1O_2$ to give endoperoxides.

It is to be expected that the role of PNA impurities should be even more pronounced for outdoor exposure conditions, where slower degradation occurs, than under our accelerated testing conditions. The atmospheric PNA concentration no doubt originates from the incomplete combustion of hydrocarbon fuels and pyrolysis of lubricants (12,15). Significant concentrations of aromatic products are emitted even from engines run on pure alkanes (25).

Despite the emphasis on possible $^1O_2$ involvement in polyolefin photodegradation, it must be stressed that in practice the photooxidation of these polymers probably results from a combination of sources ($^1O_2$, O_3 macro carbonyl and peroxide impurities, Ti residues, etc.). Consequently, the effectiveness of UV stabilizers must derive from some combination of UV absorption, excited state quenching, $^1O_2$ and O_3 scavenging, hydroperoxide thermal decomposition, and radical scavenging.

Issued as NRCC No. 13706.

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Received August 21, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 767–770 (1973)

A RELATIONSHIP BETWEEN THE VOLUME AND CHEMICAL STRUCTURE AT THE GLASS TRANSITION TEMPERATURE*

In connection with other work, we had a need to be able to estimate the critical volumes of low molecular weight liquids as a function of molecular weight and chemical structure. However, critical volumes have been measured experimentally for only a relatively few liquids. For this reason, several schemes for estimating critical volumes from a knowledge of the chemical structure and other parameters such as the parachor, critical pressure, or critical temperature have been proposed (1).

We were able to develop an alternative system of additive group contributions from which the critical volumes of liquids could be estimated from a knowledge of the chemical structure alone.

The group contributions developed here are listed in Table I. The critical volume (per mole), V_c, is estimated using the relationship,

$$V_c = \Sigma v_{ci} \tag{1}$$

where the v_{ci} are the group contributions for the appropriate structural and chemical features listed in Table I. The V_c values for some 134 liquids which differed widely in chemical structure could be estimated with an average error of 1.88%; marked deviations, when they do occur, are usually limited to the first few members of a homologous series.

During this time we also discovered a paper by Sugden (2) which was concerned with the estimation of the molar volumes of low molecular weight liquids at absolute zero, V_o, based on the equation

$$\rho = \rho_0 \left(1 - \frac{T}{T_c}\right)^{0.3} \tag{2}$$

where ρ and ρ_0 are the orthobaric densities at the temperature T and at absolute zero, respectively, and T_c is the critical temperature. Sugden was also able to show that the molar volumes for various low molecular weight liquids at absolute zero (obtained from the molecular weight and the derived value of ρ_0) are also additive functions of the chemical structure and composition. For temperatures below the normal boiling point, the orthobaric density can be taken equal to the density of the liquid phase. The molar volume at absolute zero is estimated using the following relationship,

*This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

TABLE I

Group and Atomic Contributions to the Molar Volume at the Critical Temperature

Group	v_{ci}, cc/mole
CH_3	70.1
CH_2	57.5
CH	43.2
C	22
CH_2=	67.2
CH=	48.0
>C=	38.0
≡CH	56.5
≡C–	37.0
3-membered ring	-20.0
4-membered ring	-20.0
5-membered ring	-27.5
6-membered ring	-37.0
conjugation	6.0 per each double bond
C=O	64.3
CO_2	91
HCO (formate)	101
COOH	103
NH_2	11 (aromatic)
NH	46
-N=	39.0
CN	102.5
S	61.7
SH	77.0
OH	24.3
O	20.0
F	43.0
F	33.9 (each for 2 on same carbon)
F	42.0 (each for 3 on same carbon)
CF_2	85.0 fluorocarbons only
CF_3	110.0 fluorocarbons only
Cl	69 (49 aromatic)
Cl	63 (each for 2 on same carbon)
Cl	58 (each for 2 on same carbon)
Br	87.5 (65 aromatic)
I	157.0 (92 aromatic)

$$V_o = \Sigma v_{oi} \tag{3}$$

where the v_{oi} are the additive group contributions obtained from ref. (2).

With this background, it occurred to us that the total free space defined as $V_c - V_o$, i.e., the total volume change on going from $T = 0$ to $T = T_c$, and which now can be estimated from a knowledge of the chemical structure alone, might have some relationship to the volume at the glass transition temperature, T_g. Accordingly, we examined data from the extensive compilation of Sharma, Mandelkern, and Stehling (3). It was found that the following relationship could be applied to the data from Ref. (3) (except for the materials for which no estimates of either V_o or V_c could be obtained),

$$\frac{V_g}{V_c - V_o} = K \tag{4}$$

where V_g is the molar volume of the low molecular weight liquid or the volume of the repeating unit for high molecular weight polymers at the glass transition temperature. For some 28 polymers with glass transition temperatures ranging from 130° to 488°, the value of K is 0.369 with a standard deviation of 0.0178.

Bondi (4) pointed out earlier that for five polymers the volume ratio defined by $V_g - V_o{}^*/V_g$ was nearly constant with an average value of 0.130 and a standard deviation of 0.0058. Here $V_o{}^*$ is the volume of the substance in the crystalline phase at absolute zero. Values of $V_o{}^*$ can be estimated from a knowledge of the chemical structure and additive group contributions listed in ref. (5). The numerator of Bondi's volume ratio represents the volume at T_g in excess of the volume required for molecular motions. Using the data from ref. (3), the ratio has been evaluated for 16 polymers (values for other polymers could not be estimated since the requisite $V_o{}^*$ contributions had not yet been reported) and had the value 0.123 with a standard deviation of 0.0342.

Bondi (4) also considered values of the ratio $V_g - V_w/V_g$ where V_w is the van der Waals volume at absolute zero which can also be estimated from a knowledge of the chemical structure and additive group contributions (5). The numerator here represents the maximum change in volume on going from T_g to absolute zero. Bondi found the ratio to have the value of 0.343 with a standard deviation of 0.0207. Using data in ref (3), we have evaluated this ratio for 27 polymers (values for other polymers could not be estimated because the necessary V_w increments were not available) and the value was found to be 0.356 with a standard deviation of 0.0277. Thus, although Bondi has obtained correlations between the van der Waals volume at absolute zero and the volume at T_g, we have shown that as good or better a correlation can also be obtained between the total volume change on going from $T = T_c$ to $T = 0$ and V_g.

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Received June 11, 1973
Revised October 8, 1973

POLYMER LETTERS EDITION VOL. 11, PP. 771-776 (1973)

THE YOUNG'S MODULUS OF POLYETHYLENE

Introduction

Although it has been known for some years that the major morphological feature of an unoriented crystalline polymer is a spherulite consisting of radiating lamellar crystals, no study has been reported of the effect of the two major independent variables, spherulite radius and lamellar thickness, on the mechanical properties of a polymer. Some work has been reported on the effects of spherulite size on the impact strength of polyethylene (1), the mechanical properties of nylon 66 (2), the brittleness of polychlorotrifluoroethylene (3), and the yield and fracture stresses of polypropylene (4). Little of the reported work has utilized a true stress-true strain analysis of the experimental data.

The spherulite radius may be controlled by a suitable choice of supercooling during crystallization thereby determining the nucleation density. The lamellar thickness is first determined by the supercooling, but may be controlled (5), within certain bounds, by later annealing procedures.

In the present communication we wish to report the variation of the Young's Modulus of high density polyethylene with both spherulite size and lamellar thickness. The experimental results are interpreted using the theory of fibre-reinforcement proposed recently by Halpin and Kardos (6). This work is part of a more extensive program of research investigating the effects of the variables on all major mechanical properties of polyethylenes which will be reported in greater detail shortly.

Experimental

The material used was a standard high-density polyethylene (M_N = 10,700; M_W = 106,000) supplied by the Polymer Supply and Characterisation Centre at the Rubber and Plastics Research Association, Shawbury, Salop.

Dumbbell shaped specimens were cut out of a compression-moulded sheet and placed in close-fitting moulds. These moulds were heated to 200°C in a vacuum for two hours before quenching to the desired crystallization temperature. Samples were then crystallized for 24 to 36 hours, dependent on the temperature. In order to produce specimens of small spherulite size, repeated quenching from a temperature just above the melting point was used which increased the nucleation density by self-seeding. The specimens were polished using a series of graded emery papers until a reproducible surface had been produced.

Mechanical properties were determined using an Instron tester at 23°C and a cross-head speed of 0.05 cm min^{-1}. Results were averaged over six specimens

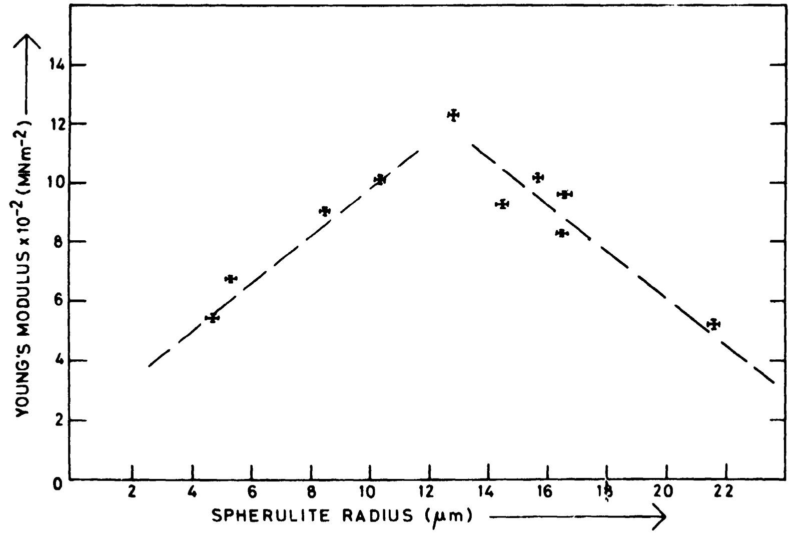

Fig. 1. Graph of Young's Modulus versus spherulite radius for high-density polyethylene.

true stress-true strain analysis of Instron chart data being used throughout. The Young's Modulus was then obtained over the first 1% of strain.

Spherulite radii were determined, in the main, using laser light scattering (7), although occasional samples were also analysed using a polarizing microscope to confirm the light scattering results. Results for the two techniques never differed by more than 10%.

Lamellar thicknesses have been calculated from melting points (Dupont Thermal Analyser) and data (5) from the literature relating lamellar thickness to melting point. Results have been confirmed, for some samples, using low-angle X-ray diffraction and the maximum discrepancy was 30 Å in 450 Å.

Results and Discussion

The variation of Young's Modulus with spherulite radius for a series of 'as-crystallized' specimens is shown in Figure 1. A maximum value of 1200 MNm^{-2} occurs at a radius of 13 μm. The initial increase in modulus would normally be ascribed to increasing crystallinity. As the crystallinities of all our specimens were between the values of 75% ± 5% and 85% ± 5%, and vary in a random manner with supercooling and annealling, we may regard the crystalline fraction as essentially constant. Hence crystallinity will be excluded from our considerations. As these specimens were each produced at a unique supercooling, the lamellar thickness cannot be considered as constant over the whole range of supercoolings used. The lamellar thickness is known (5) to be approximately constant for supercoolings greater than ca. 20°C, to increase slowly between supercoolings of 20°C and 12°C, and to increase rapidly as

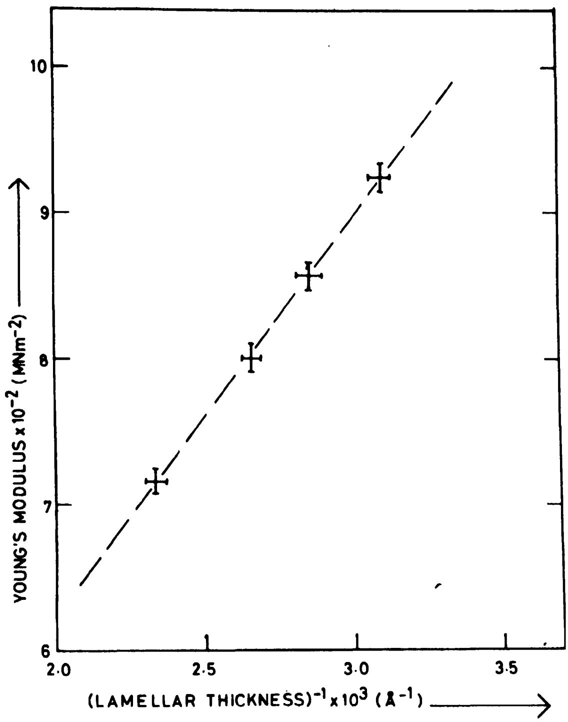

Fig. 2. Graph of Young's Modulus versus lamellar thickness for high-density polyethylene with constant spherulite radius (9 μm).

supercooling is decreased below 12°C. A supercooling of 17°C was used to produce the specimen of spherulite radius 13 μm. The negative slope of the curve beyond this point could be caused by lamellar thickness increasing as spherulite size increases.

In order to test this hypothesis, a series of specimens of spherulite radius 9.0 μm were annealed at various temperatures in order to vary the lamellar thickness while keeping the spherulite radius constant. The results of these experiments are given in Figure 2, and confirm the hypothesis that modulus is inversely proportional to the lamellar thickness.

Halpin and Kardos (6) have suggested that a spherulitic polymer may be regarded as a reinforced composite material in which the lamellae may be regarded as randomly arranged fibers or ribbons. This theory introduces the aspect ratio, (ratio of twice the length to the thickness of the ribbon) as an important variable. Hence, for a spherulitic polymer consisting of radiating lamellae, this parameter would be equated to the ratio of the spherulite's diameter to the lamellar thickness.

The experimental Young's Modulus is plotted against this aspect ratio (ξ) in Figure 3. There is at first a proportionality followed by an aspect-ratio-independent plateau region. The plateau region begins at an aspect ratio of 800.

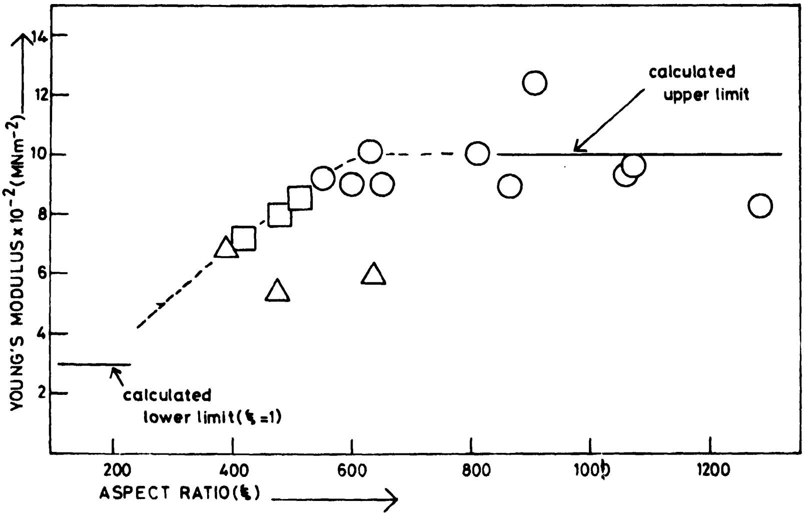

Fig. 3. Graph of Young's Modulus versus aspect ratio of lamellae. (○, slowly crystallized specimens; □, annealled specimens; and △, repeatedly-quenched specimens.)

Halpin's theory predicts that the modulus should become a constant for aspect ratios greater than ca. 1000.

This correlation may be taken as further evidence in favor of this treatment. The behavior of the specimens produced by repeated quenching does not follow the trend.

The theory of Halpin and Kardos has been calculated for a two-dimensional system. A spherulitic polymer, however, has three-dimensional misalignment of fibres, and an adaptation for a three dimensional system is necessary. To a first approximation the equation relating E to ξ for this system can be shown to be

$$\frac{3E}{E_m} = \frac{1 + \xi \eta v_f}{1 - \eta v_f} \tag{1}$$

where v_f is the volume fraction of crystalline material and

$$\eta = \frac{E_c - E_m}{E_c + \xi E_m} \tag{2}$$

In order to test the theory quantitatively it is necessary to know two additional parameters. These are the modulus E_c of the ribbon-like lamella and the modulus E_m of the amorphous matrix. The value of E_c should be that of the b-axis modulus, the highest reported experimental value of which is 3.9

GNm^{-2}. From this value, the upper limit of E at high ξ was calculated (see Fig. 3) and is in good agreement with the experiment. The value of E_m to be used is more difficult to obtain, but should be of the order of those of non-crystallizing rubbers and has been taken as 10 MNm^{-2} (cf. SBR, 7MNm^{-2}; butylrubber, 14 MNm^{-2}).

Rearranging eq. 1. we have

$$\frac{3E - E_m}{3E + E_m} = v_f \tag{3}$$

A plot has therefore been made of $(3E - E_m)/(3E + \xi E_m)$ versus η, the slope of which should equal v_f. This graph is shown in Figure 4, together with lines corresponding to the maximum (0.77) and minimum (0.67) values of volume fraction crystallinity obtained experimentally. The majority of the points derived from as-crystallized and annealed specimens fall within the bounds, whereas points derived from repeatedly quenched specimens do not. This implies that the amorphous structure is different for this case, and thus depends critically on thermal history. Changes in the structure could result in a different amorphous modulus occurring for quenched specimens due perhaps to a reduction in tie-chain concentration or to the tie chains being less constrained. The data for these specimens fit the theory if a value of E_m of approximately half that used for the other specimens is employed.

The major conclusion to be inferred from this work is that a semicrystalline

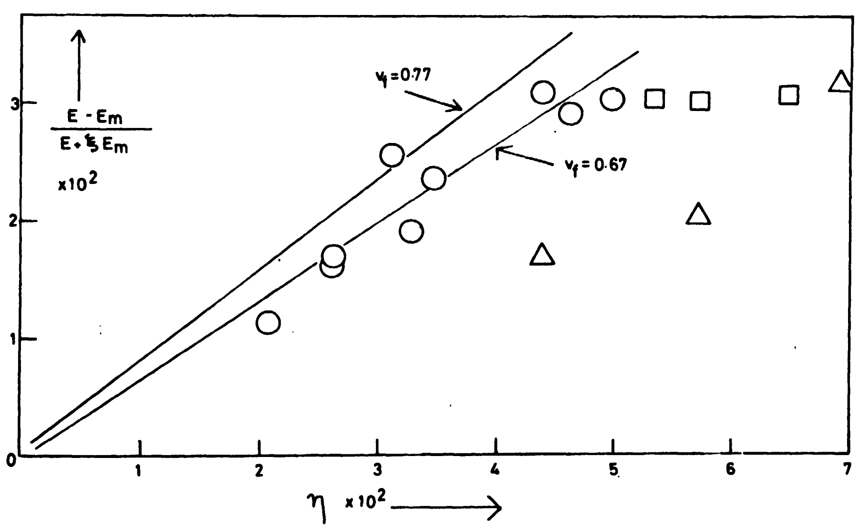

Fig. 4. Graph of $(3E - E_m)/(3E + \xi E_m)$ versus η (○, slowly crystallized specimens; □, annealed specimens; and △, repeatedly quenched specimens).

polymer with a well-defined thermal history, even a one with 80-% weight fraction crystallinity, may be regarded as a material randomly reinforced by fibres for the purpose of modulus prediction.

This work was supported by the Science Research Council and we are grateful for the award of an S. R. C. Studentship to J. P.

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Received March 29, 1973
Revised July 2, 1973

ANNOUNCEMENTS

Seventh Symposium on Plastics Processing

The Seventh Symposium on Plastics Processing will be held in Aachen, Germany, on March 20-22, 1974. The general program will consist of the following topics:

Extrusion. Extrusion of films and sheets. Fundamentals for the fully-automatic quality control in extrusion blow moulding. The processing of rigid-PVC on the single-screw extruder using an intermeshing, compulsory mixing system.

Injection Moulding. Application of process computers in injection moulding. Quality control in injection moulding by means of conventional methods. A new method for the injection moulding of fiber-reinforced UP-materials.

Material Testing. Relationship between electrical-insulation value and critical strain at high-tension insulators. Influence of corrosive liquids on thermoplastics under load. Principles for the computation of the mechanical qualities of rigid plastics foams. Nondestructive testing of large-surfaces structures by means of holographic interferometry. Adhesion and failure of organic surface-protectional layers.

Foaming. PUR-process optimization for the processer. Reaction foaming method on the basis of styrene. Demoulding of PUR-mouldings.

Reinforcing. Methods for the control and analysis of the compressing phase during compressing resin mats (sheet moulding).

Designing. Systematic development of new plastic products.

Teaching. Industrial training in the plastics processing industries—problems and possible solutions.

International Wool Textile Research Conference

The next International Wool Textile Research Conference is currently being organized by the Deutsches Wollforschungsinstitut, e.V., of the Technische Hochschule of Aachen and will take place in Aachen on September 2-11, 1975. At this conference, wool research scientists from all over the world will exchange ideas and experiences, discuss the current state of basic research, and make suggestions for improvements in the area of applied wool research. It is proposed that the results of research on wool/man-made fibre blends will be discussed along with the problems related to pure wool. In this way the conference should serve as an instrument for the exchange of information between industry and research.

The scientific programme for the conference consists of:

1. Reviews – nine invited speakers will outline the current state of wool science and technology.
2. Discussion papers – these can be submitted by all those wishing to participate and will include the work of scientists and technologists in basic and applied research on wool, mohair, blends, and hair cosmetics. At present, approximately 250 papers have been submitted.
3. Round table discussions – the treatment of more specialized topics will take place in small groups; also giving time to continue discussion of original contributions for which the time allowed was not sufficient.
4. Plenary lectures – prominent speakers will be invited to discuss generally interesting subjects from science or economics.

Anyone interested in this conference can obtain information, registration form, and a tentative list of topics from the Deutsches Wollforschungsinstitut, 5100 Aachen, Veltmanplatz 8.

Conference on Laboratory Instruction in Chemistry

Rensselaer Polytechnic Institute, under the sponsorship of the International Union of Pure and Applied Chemistry, will host a three-day conference on Laboratory Instruction in Chemistry, to be held in Troy, New York, on June 10-12, 1974. Five major areas, each keynoted by a plenary lecturer and supported by panel discussions and contributed papers are planned in the following areas:

The Integrated Laboratory in Chemistry
The General Chemistry Laboratory
The Computer in Laboratory Instruction
Instructional Aids and Equipment
Laboratory Organization

The objectives of this conference are to examine critically the role of direct student experimentation and the format of the laboratory organization in view of the demands of sophisticated equipment, student time, space, etc., and the relation of the laboratory to the overall trends in Chemical education. The format of the conference will be informal, and will provide opportunity for participants to evaluate past, present, and future aspects of laboratory instruction, to exchange views and experiences, and to explore direction and innovation.

The conference will be part of the 150th anniversary activities of Rensselaer Polytechnic Institute. Founded in 1824, Rensselaer initiated the incorporation of field work and laboratory studies in a regular course of science in the United States.

Further information may be obtained by writing to the Chairman of the Organizing Committee, Dr. Robert L. Strong, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181.

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Polymer Letters Edition

JOURNAL OF POLYMER SCIENCE

Volume 11, 1973

An Interscience® Publication
Published by JOHN WILEY & SONS

Statement of ownership, management, and circulation (Act of August 12, 1970: Section 3685, Title 39 United States Code)

1. Date of filing: October 1, 1973
2. Title of Publication: JOURNAL OF POLYMER SCIENCE
3. Frequency of issue: monthly
4. Location of known office of publication: John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016
5. Location of headquarters of general business offices of publisher: John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016
6. The names and addresses of publisher, editor, and managing editor:
Publisher: John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10016
Editor: Herman Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201, C. G. Overberger, Dept. of Chemistry, Univ. of Michigan, Ann Arbor, Mich. 48104, and T. G Fox, Carnegie-Mellon Institute, 4400 Fifth Ave., Pittsburgh, Pennsylvania 15213
Managing Editor: None
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